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Matrix Isolation, Zero-Field Splitting Parameters, and Photoreactions of Septet 2,4,6-Trinitrenopyrimidines

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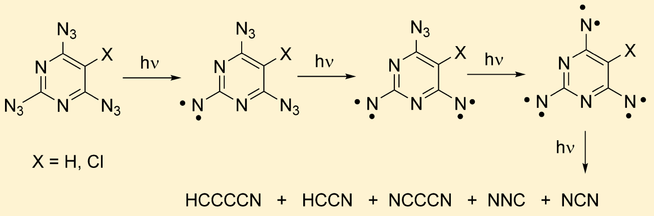
S Supporting Information



ABSTRACT: The key intermediates of decomposition of high-energy 2,4,6-triazidopyrimidine and its 5-chloro-substituted derivative, the detonation of which is used for preparation of carbon nitrides, were investigated using electron paramagnetic resonance (EPR) spectroscopy in combination with quantum chemical calculations. The decomposition of the triazides was carried out photochemically, using the matrix isolation technique. The photodecomposition of both triazides with 254 nm light in argon matrices at 5 K occurred selectively to subsequently give the corresponding triplet 4,6-diazido-2-nitrenopyrimidines, quintet 4-azido-2,6-dinitrenopyrimidines, and septet 2,4,6-trinitrenopyrimidines. The latter were photochemically unstable and decomposed to form triplet nitrenes NCN and NNC as well as triplet carbenes NCCCN, HCCN, and HCCCCN. The results obtained provide important information about exchange interactions in high-spin nitrenes with the pyrimidine ring and the mechanism of the formation of carbon nitrides during thermolysis of 2,4,6-triazidopyrimidine.

INTRODUCTION

The first high-spin arylnitrenes were characterized more than 40 years ago by Wasserman and co-workers using electron paramagnetic resonance (EPR) spectroscopy. Quintet *meta*-phenylenedinitrene[1] and septet 2,4,6-tricyanophenylenetrinitrene[2] were generated by photolysis of the corresponding di- and triazides in frozen 2-methyltetrahydrofuran (MTHF) solutions. However, the assignment of all signals in the complex EPR spectra and the determination of the zero-field splitting (ZFS) parameters of these high-spin nitrenes became possible only recently with the help of modern line-shape spectral simulations programs and quantum chemical calculations of the ZFS parameters.[3,4] Highly reactive nitrenes such as septet 2,4,6-trinitreno-s-triazine (**1**),[5] 2,4,6-trinitreno-3,5-dicyanopyridine (**2**),[6] or 2,4,6-trinitreno-3,5-difluoropyridine (**3**)[7] are not stable in organic glasses and therefore could not be detected in these media.[8] Matrix isolation spectroscopy in solid rare gases, on the other hand, made it possible to obtain EPR of highly reactive oligonitrenes and in some cases even record IR spectra of these elusive species (Scheme 1). Using these techniques, the septet trinitrenes **1**−**12** and a large number of quintet dinitrenes could be characterized by EPR spectroscopy in the past decade.[4−7,9]

The aryloligonitrenes characterized so far are substituted benzene, pyridine, or 1,3,5-triazine rings, whereas pyrimidylnitrenes remained unexplored, so far. In analogy to other aryloligoazides, the photolysis of the pyrimidyltriazides **13a** or **13b** could principally produce mixtures of the triplet nitrenes **14a**, **14b**, **15a**, and **15b**, quintet dinitrenes **16a**, **16b**, **17a**, and **17b**, and septet trinitrenes **18a** and **18b** (Scheme 2). The subsequent photolysis of these oligonitrenes is expected to result in the cleavage of the aromatic ring system and formation of small, highly unsaturated radicals. These radicals might be the source of nanotubes that are formed during the explosive decomposition of **13a**.[10] Here, we describe the photolysis of triazides **13a** and **b** in solid argon studied by EPR spectroscopy in combination with density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

I. Matrix Photolysis of Triazides 13a and b. Short-term UV irradiation (5 min, λ = 254 nm) of triazides **13a** or **b**, matrix-isolated in argon at 5 K, led to the appearance of EPR signals of triplet, quintet, and septet nitrenes in the 0−9000 G region (Figures 1a and 2a). After prolonged UV irradiation (70 min) of the matrix containing triazide **13a**, EPR signals of the quintet and septet nitrenes almost completely decayed, leaving only the signals of six triplet biradicals in the region between 6200 and 8200 G (Figure 1b). In contrast, prolonged UV irradiation (70 min) of matrix-isolated triazide **13b** resulted only in the partial decay of EPR signals of quintet and septet nitrenes, and in the growth in intensity of three EPR signals at 6930, 7300, and 8200 G (Figure 2b). These results demonstrate that high-spin pyrimidylnitrenes are photochemically unstable and in a sequence of photochemical steps decompose to triplet diradicals. The nitrenes bearing a chlorine atom on the pyrimidine ring are markedly more stable.

II. Identification of Paramagnetic Products. The line-shape spectral simulations (Figure 1c) in combination with

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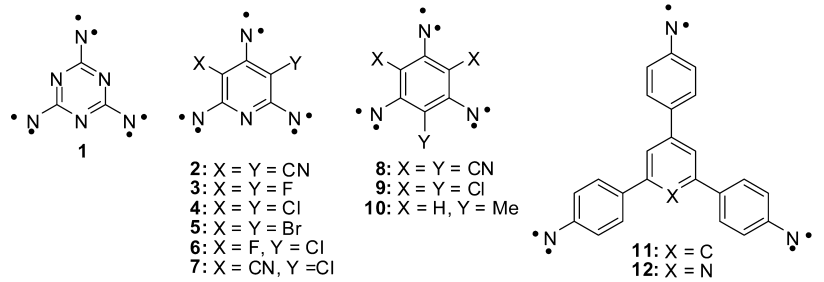
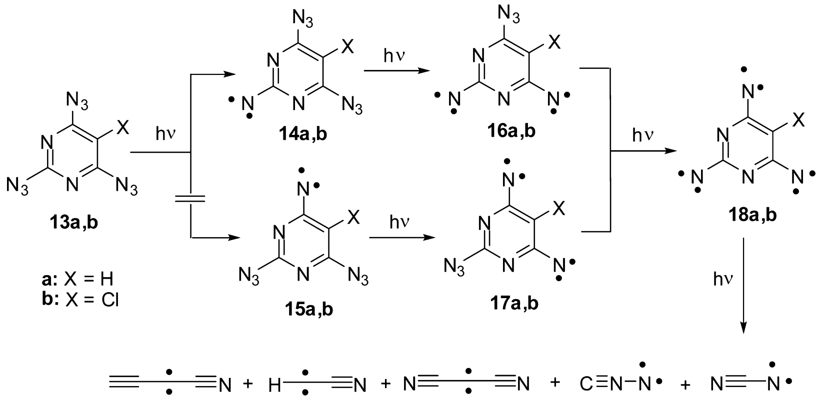
Scheme 1



Scheme 2



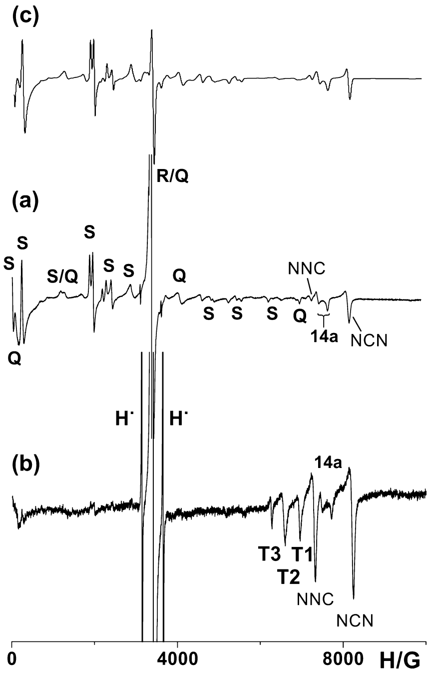


Figure 1. EPR spectra obtained after (a) 5 min, (b) 70 min of UV irradiation of triazide **13a**. (c) Simulation for a mixture of **14a**, **16a**, **18a**, NCN, and NNC in the ratio 35:35:5:22:3, respectively. The signals are assigned to triplet (T), quintet (Q), septet (S) nitrenes, doublet radicals (R), and hydrogen atoms (Ḣ) formed as byproducts of the photolysis. Microwave frequency: (a) 9.59226 GHz; (b) 9.59224 GHz.

DFT calculations of the ZFS parameters (Tables 1 and 2) show that the EPR spectrum in Figure 1a represents a superposition of EPR signals of five paramagnetic species: triplet nitrene NCN, triplet nitrene **14a**, triplet nitrene NNC, quintet dinitrene **16a**, and septet trinitrene **18a** in a ratio of 22:35:3:35:5. The EPR spectrum in Figure 1b is a superposition of EPR signals of six triplet species: triplet nitrene NCN, triplet nitrene **14a**, triplet nitrene NNC, triplet carbene NCCCN (**T$_1$**), triplet carbene HCCN (**T$_2$**), and triplet carbene HCCCCN (**T$_3$**) in a ratio of 33:16:24:9:14:4. Similar paramagnetic products (**14b**, **16b**, **18b**, NCN, NNC, and NCCCN) are also formed during the photolysis of triazide **13b** (Table 3). The assignment of all lines in the EPR spectra of nitrenes **16a**,**b** and **18a**,**b** as well as experimental and theoretical EPR spectra for mixtures of NCN, NNC, NCCCN, HCCN, and HCCCCN at early and late stages of the photolysis of triazide **13a** are discussed in the Supporting Information.

The formation of the triplet nitrenes **14a** and **14b**, NCN, and NNC, as well as of the triplet carbenes NCCCN, HCCN, and HCCCCN is convincingly confirmed by comparison with the literature data[5,11−14] and by quantum chemical calculations (Tables 1 and 2). For triplet pyrimidyl-2-nitrene D_T = 1.217 cm^{-1} and E_T = 0.0052 cm^{-1}, and for triplet pyrimidyl-4-nitrene D_T = 1.194 cm^{-1} and E_T = 0.0012 cm^{-1} were reported in the literature.[14] The large difference in the D_T values of the triplet nitrenes **14a**, **14b**, and **15a**, **15b** is also predicted by quantum chemical calculations (Table 1), which excludes overlapping of EPR signals of these species. The experimentally determined D_T values nicely fit the calculated D_T values of triplet nitrenes **14a** and **14b** (Table 1).

For the first time, triplet NCN and NCCCN were detected by EPR spectroscopy during the photolysis of azidocyanide and diazomalononitrile in solid organic solutions.[11] On prolonged UV irradiation, triplet NCN rearranged into triplet NNC. Later, triplet NCN, NNC, and NCCCN were detected by EPR spectroscopy as products of the photodecomposition of septet trinitrene **1** in nitrogen matrices.[5] Taking into account that **18a** and **18b** contain the same N═C(N)—N fragment as **1**, it is

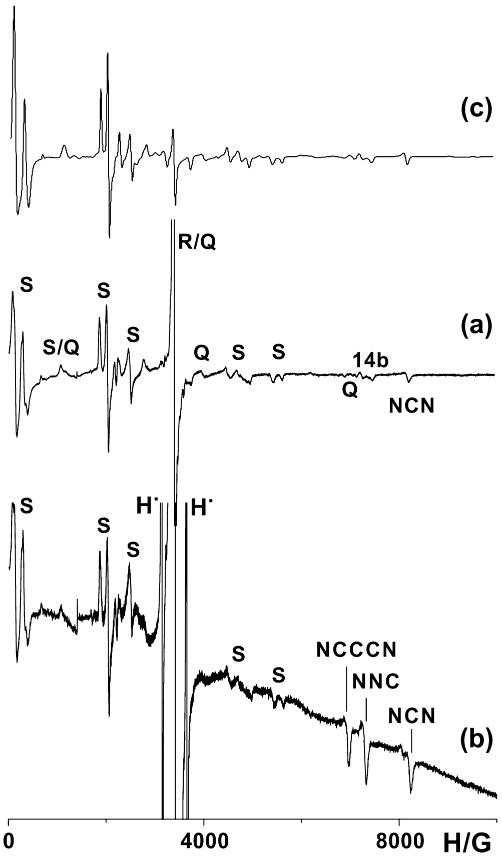


Figure 2. EPR spectra obtained after (a) 5 min, (b) 70 min of UV irradiation of triazide **13b**. (c) Spectrum simulated for a mixture of **14b**, **16b**, **18b**, and NCN in a ratio of 4:3:3:2. The signals are assigned to triplet (T), quintet (Q), septet (S) nitrenes. Doublet radicals (R) and H atoms (Ḣ) are byproducts of the photolysis. Microwave frequency: (a) and (c) 9.59208 GHz; (b) 9.59224 GHz.

not surprising that photodecomposition of **18a** and **18b** in solid argon also leads to triplet NCN, NNC, and NCCCN.

Triplet HCCN was observed by EPR spectroscopy as a product of the photolysis of diazoacetonitrile.[12] The D_T and E_T values of this carbene nicely fit the experimentally determined and theoretically predicted D_T and E_T values (Table 2) of one of the triplet products formed during the photodecomposition of septet trinitrene **18a** (Scheme 3). In principal, the photodecomposition of septet trinitrene **18b** could also lead to carbene ClCCN, which is expected[15] to show a singlet ground state. Therefore, even if it were formed, it would not be detected in our EPR experiments.

Table 2. Experimental and Theoretical Parameters *D* and *E* in cm^{-1} for the Small Triplet Molecules

diradical	experiment[a] *D*	theory[b] *D*	experiment[a] *E*	theory[b] *E*
NCN	1.545[c,d]	1.502	0.000[c,d]	0.0000
	1.535[e]		0.000[e]	
NNC	1.153[c,d]	1.137	0.000[e]	0.0000
	1.145[e]		0[e]	
NCCCN	1.002[d]	1.006	<0.002[d]	0.0000
	1.000[e]		0.000[e]	
HCCN	0.8629[f]	0.910	<0.001[f]	0.0304
	0.8700[e]		0.0017[e]	
HCCCCN	0.7814[g]	0.797	0.000[e]	0.0000
	0.7600[e]			

[a] In argon matrices, if not specified otherwise. [b] Spin-unrestricted SVWN3/6-311++G(d,p) calculations (see computational details in the Experimental section). [c] ref 5. [d] In fluorolube suspension, ref 11. [e] This work. [f] In polychlorotrifluoroethylene, ref 12. [g] In gas phase, ref 13.

Triplet carbene HCCCCN has so far not been generated in a laboratory, but was recently detected as a component of interstellar matter.[16] The D_T parameter of HCCCCN in gas phase was estimated as 0.7814 cm^{-1}.[13] This value agrees very well with the data derived from our EPR spectrum (Table 2). A theoretical study suggests that HCCCCN can be formed by the reaction of carbon atoms with HCCCN.[17] In our experiments, we observe NNC, which may decompose to carbon atoms and molecular nitrogen.[18] In addition, trinitrene **18a** can undergo a sequence of photochemical rearrangements to form HCCCN (Scheme 3). Similar photochemical reactions have been described recently for nitrenotriazines.[19] Thus, the formation of HCCCCN during the photodecomposition of septet trinitrene **18a** can be explained by the photoreaction of HCCCN with carbon atoms.

III. Selective Photolysis of the Azido Groups in Triazides 13a and b. The formation of triplet nitrenes **14a** and **b** during the initial photolysis of triazides **13a** and **b** indicates that this photochemistry is selective. Similar selective photodissociations of α-azido groups have been observed previously during the matrix photolysis of various 2,4,6-triazidopyridines.[9c,20] These selective reactions were explained in terms of photodynamically controlled dissociation processes.[21] Short-wavelength UV irradiation (λ < 280 nm) of aromatic polyazides results in the population of high-energy singlet excited states that rapidly undergo diabatic dissociation

Table 1. Experimental and Theoretical *D* and *E* Values in cm^{-1}, and Theoretical *g*-Factors for Nitrenes 14−18

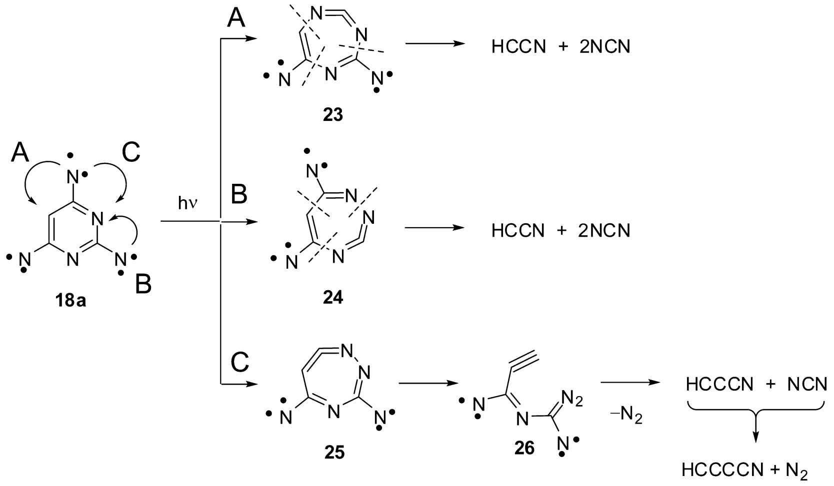
nitrene	experiment |*D*|	theory[a] *D*	experiment |*E*|	theory[a] *E*	theory[a] *g*
14a	1.260	1.271	0.0046	0.014[b]	2.0033
14b	1.170	1.162	0.0044	0.021[b]	2.0042
15a	–	1.218	–	0.020[b]	2.0033
15b	–	1.121	–	0.020[b]	2.0041
16a	0.241	0.251	0.054	0.050	2.0033
16b	0.231	0.236	0.054	0.050	2.0039
17a	–	0.256	–	0.042	2.0034
17b	–	0.254	–	0.039	2.0040
18a	0.1122	−0.1146	0.0035	−0.0037	2.0033
18b	0.1119	−0.1127	0.0058	−0.0065	2.0038

[a] Spin-unrestricted SVWN3/6-311++G(d,p) calculations (see computational details in the Experimental section). [b] The calculations significantly overestimate the *E* parameters of triplet nitrenes (see Table S1 in the Supporting Information).

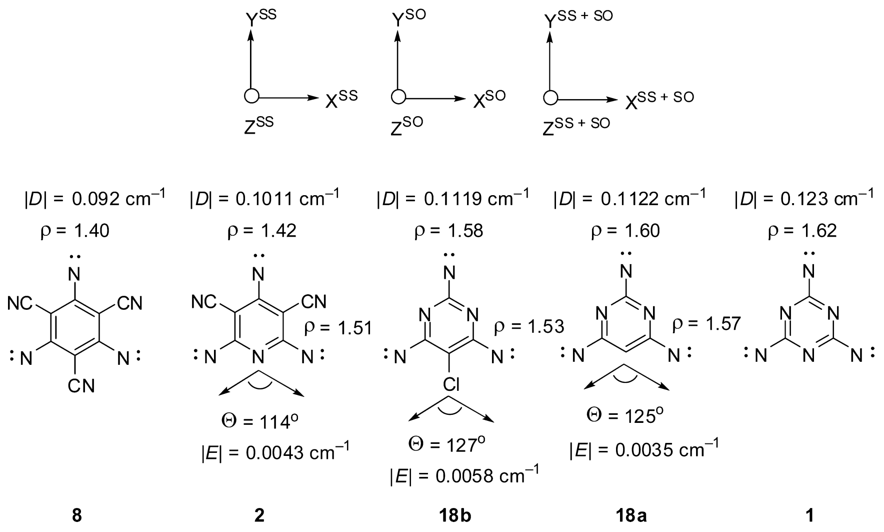
Table 3. Relative Yields of Nitrenes and Carbenes at Different Stages of Photolysis of Triazides 13a and b

azide	time (min)	relative yields (%)							
		14	**16**	**18**	NCN	NNC	NCCCN	HCCN	HCCCCN
13a	5	35	35	5	22	3	–	–	–
	70	16	–	–	33	24	9	14	4
13b	5	33	25	25	17	–	–	–	–
	70	–	–	11	27	35	27	–	–

Scheme 3



Scheme 4



of the $N-N_2$ bonds to form the corresponding singlet mononitrenes. The latter then undergo intersystem crossing to form more stable triplet mononitrenes. Previous studies have shown that the $N-N_2$ bonds in the α-azido groups of 2,4,6-triazidopyridines and in the 2-azido groups of pyrimidines possess the highest bonding orbital density.[21,22] Therefore, the local excitation of these groups should produce excited singlet states S_{n-m}*. The energies of these states are very similar to the energy of the excited states S_n* formed by $\pi-\pi$* excitation of the aryl moiety of azides after short-wavelength UV irradiation. Internal conversion from S_n* leads to the S_{n-m}* states that preferentially undergo fast dissociation of the $N-N_2$ bonds. Such effects are well documented in the literature as "photodynamically controlled dissociation processes" (for a qualitative diagram of the excited states responsible for the fast diabatic and slow adiabatic photodissociations of the azido groups in aromatic polyazides see Figure S10, Supporting Information).[23]

IV. Effect of the Aromatic Ring on Properties of Septet Trinitrenes. Scheme 4 shows the Mulliken spin densities (ρ) on the nitrene units of the pyrimidine derivatives **18a** and **b**, the benzene derivative **8**, the pyridine derivative **2**, and the 1,3,5-triazine derivative **1**.

By increasing the number of nitrogen atoms in the aromatic rings of trinitrenes **8**, **2**, **18a**, **18b**, and **1**, the spin density is becoming more localized at the nitrene units, and the magnetic anisotropy (D_S values) of these species is increasing. The D_S value of trinitrene **18a** is approximately 10% smaller than that of trinitrene **1**, and by 10% larger than that of trinitrene **2**. Although X-band EPR spectra of trinitrenes **18a** and **b** cannot provide information about the sign of the *D* values of these hexaradicals, numerous DFT[9,24] and ab initio[25] calculations suggest a negative sign of *D* for trinitrenes **1**, **2**, **8**, **18a**, and **b** as well as a negative sign of *E* for the C_{2V} symmetrical trinitrenes **2**, **18a** and **b**. All these trinitrenes show the same orientations of the principal magnetic axes for the tensors of the spin−spin (D^{SS}) and spin−orbit (D^{SO}) couplings, that coincide with the principal magnetic axes of the total tensor D^{SS+SO} (Scheme 4). These rules are violated only for high-spin nitrenes bearing heavy bromine or iodine atoms.[25c] For such molecules, only high-level ab initio calculations should be used to correctly predict the signs of the *D* and *E* parameters. High-spin nitrenes with negative *D* values possess magnetism and are of considerable interest as models of single molecular magnets.

The magnetic parameters of high-spin nitrenes built from light atoms depend on the angle Θ and spin populations on the nitrene units (Scheme 4). Thus, for the C_{2V} symmetric trinitrenes **2**, **18a**, and **18b**, which contain two equivalent nitrene units with $D_{t1} = D_{t2} = D_t$ and a third triplet unit with $D_{t3} = D_t\ (1 + \lambda)$ where $\lambda = (\rho_3 - \rho_1)/\rho_1$, the ratio E_S/D_S is a function of the angle Θ and the parameter λ:

$$|E_S/D_S| = |3^{1/2}\Delta\Theta + \lambda|/3 \qquad (1)$$

where $\Delta\Theta = (2\pi/3 - \Theta)$ and $|\Delta\Theta| \ll 1$.[6] The first term in eq 1 is due to the deviation of Θ from 120°, and the second term results from the nonequivalence of the triplet units in C_{2V} symmetrical septet molecules. Thus, D_{3h} symmetrical trinitrenes **1** and **8** with $D_{t1} = D_{t2} = D_{t3}$ and $\Theta = 120°$ show a value of $E_S = 0$ cm^{-1}.[4,5] The E_S values of C_{2V} symmetrical trinitrenes **2**, **18a**, and **18b** nicely illustrate the dependence of these values from Θ and λ.

The constitution of the aromatic ring also affects the yield and the photochemical stability of septet trinitrenes. Septet trinitrenobenzenes are obtained almost quantitatively, and are very stable toward UV irradiation.[2,4,9c] Septet 2,4,6-trinitrenopyridines are photochemically also rather stable, but the photodissociation of the azido groups in the precursors is rather inefficient, and thus they are formed in only 5−10% yields.[6,7,9c] In contrast, the low yields of the septet trinitrenes **1** and **18a** result from the low photochemical stability of these species. The chlorine atom in position 5 of the pyrimidine ring increases the stability of **18b** compared to **18a** by approximately a factor of 5.

■ CONCLUSIONS

Triplet, quintet, and septet nitrenes formed during the photolysis of triazides **13a** and **b** were isolated in argon matrices and characterized by EPR spectroscopy. EPR spectral simulations in combination with quantum chemical calculations reveal that the 254 nm photolysis of matrix-isolated **13a** and **b** is selective and successively produces triplet mononitrenes **14a** and **b**, quintet dinitrenes **16a** and **b**, and septet trinitrenes **18a** and **b**. The D_S values of the septet trinitrenes **18a** and **b** significantly exceed the D_S values of septet 2,4,6-trinitrenobenzenes and 2,4,6-trinitrenopyridines, but are smaller than that of septet 2,4,6-trinitreno-s-triazine. These effects are associated with stronger dipolar spin−spin interactions in septet trinitrenes containing a larger number of nitrogen atoms in the aromatic ring. Similarly to 2,4,6-trinitreno-s-triazine, trinitrene **18a** is photochemically unstable and decomposes to triplet nitrenes NCN and CNN as well as to the triplet carbenes NCCCN, HCCCN, and HCCCCN. The highest yield of trinitrene **18a** (about 5% relative to other paramagnetic products) is observed during the initial stages of the photolysis. In contrast, the highest yield of trinitrene **18b** reaches 25% and is reduced to 11% on prolonged UV irradiation.

The results described here provide also important information on the mechanism of the formation of carbon nitrides. Early studies[26] have shown that the thermal decomposition of cyanuric triazide produces dicyanide NCCN. More recent studies describe that the pyrolysis of cyanuric triazide can be used to prepare C_3N_4 carbon nitride nanomaterials.[27] Depending on the thermolysis conditions, the nitrogen-rich nanomaterials are obtained in the form of nanotubes, nanospheres, or nanolayers. These materials possess unique mechanical, chemical, optical, and tribological properties, including low density, extreme hardness, surface roughness, wear resistance, chemical inertness, and biocompatibility.[28]

Using the matrix isolation technique, we are now able to show that the stepwise decomposition of cyanuric triazide results in the successive formation of triplet mononitrenes, quintet dinitrenes, septet trinitrene **1**, and finally NCN and NNC.[18] The formal reaction of two molecules NCN with a molecule of NNC produces dicyanocarbodiimide NC—N═C═N—CN and N_2. Very recently, the C_3N_4 carbon nitrides have also been obtained by detonative thermolysis of triazide **13a**.[10] The results presented here suggest that the stepwise decomposition of both cyanuric triazide and triazide **13a** result in the same final products NCN and NNC, which are the direct precursors of C_3N_4 carbon nitrides.

■ EXPERIMENTAL SECTION

Synthesis. Triazides **13a** and **b** were synthesized according to literature procedures.[10]

EPR Measurements and Analysis. X-band EPR spectra were recorded on a standard X-band EPR spectrometer. The experimental technique for matrix isolation used in this study was similar to that described earlier.[6]

Solid argon matrices doped with triazides **13a** and **b** were prepared by vacuum codeposition of two separate molecular beams (Ar and triazides **13a** and **b** vapor) on the tip of an oxygen-free high-conductivity copper rod (75 mm length, 3 mm diameter) cooled at 5 K. Compounds **13a** and **b** were sublimed at 60 °C. The matrix-isolated samples were irradiated with 254 nm light of a high-pressure Hg lamp, and spectra were recorded at various irradiation times.

The computer simulations of EPR spectra were performed with the *EasySpin* program package (version 4.5.1).[29] The simulations were performed by using a matrix diagonalization method for *S* = 1, 2, or 3 using the parameters *g* = 2.003, line widths Δ*H* = 80 G for *S* = 1, and Δ*H* = 30 G for *S* = 2 and 3, line-broadening parameters Γ = 240, 60, 60, and 30 MHz for the D_Q, E_Q, D_S, and E_S values, respectively, and microwave frequencies 9.59226, 9.59224, 9.59208, and 9.59224 GHz for EPR spectra in Figure 1a,b and 2a,b, respectively.

Computational Methods. The molecular geometries of heteroaromatic nitrenes were optimized by density functional theory (DFT), using the B3LYP functional[30] and the 6-311++G(d,p) basis set.[31] These calculations were performed with the Gaussian 09 program package.[32] Tight optimization convergence criteria and an ultrafine integration grid were specified. Possible Ar−N_3 single bond rotational isomers of the triplet and quintet nitrenes containing azido groups were analyzed by this method to select the most stable conformer for use in subsequent calculations. The geometries of triplet radicals NCN, NNC, NC_3N, HC_2N, HC_4N, and HC_5H were computed using the orbital-optimized second-order Möller−Plesset perturbation theory within the resolution of the identity approximation (OO-RI-MP2)[33] and the correlation consistent basis set cc-pVTZ[34] together with the corresponding auxiliary basis set. The OO-RI-MP2 calculations were performed with the ORCA program package (version 3.0.1).[35]

The resulting structures were then used to calculate the zero-field splitting (ZFS) tensors with the ORCA package. The spin density matrix derived from a single-point spin-unrestricted DFT calculation was applied to assess the ZFS tensor. The single-point calculations were performed using the 6-311++G(d,p) basis set and the local spin density functional SVWN3 combining the Slater exchange[36] and the Vosko−Wilk−Nusair formula III correlation.[37] The ZFS tensor and parameters D and E were computed with the EPRNMR program in the ORCA package. The spin−spin coupling contribution to the ZFS was estimated by the equation of McWeeny and Mizuno.[38] The Pederson−Khanna method[39] was employed to assess the spin−orbit coupling contribution. The performance of this theoretical approach to predicting the D and E parameters of organic radicals was tested on a reference set of triplet, quintet and septet nitrenes (see Table S1 in the Supporting Information). It should be noted that similar calculations with the use of gradient-corrected functionals instead of SVWN3 significantly overestimated the parameter D.

The atomic spin densities reported herein were derived from the single-point SVWN3/6-311++G(d,p) calculations using the Mulliken population analysis.[40]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

EPR spectra of triplet products in the photolysis of triazide **13a**, EPR spectral simulations for quintet dinitrenes **16a** and **b** and septet trinitrenes **18a** and **b** at different values of the line-broadening parameters Γ, Cartesian coordinates and absolute energies for the calculated molecular structures, results of ZFS calculations for a reference set of organic radicals, program inputs for computing the ZFS parameters, UV−vis absorption spectra of triazidopyrimidines **13a** and **b**, and results of excited state calculations for triazidopyrimidine **13a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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