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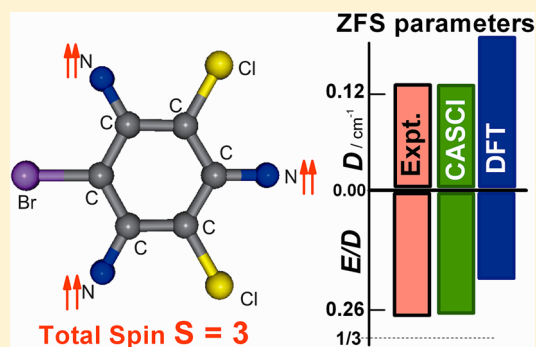
Heavy Atom Effect on Magnetic Anisotropy of Matrix-Isolated Monobromine Substituted Septet Trinitrene

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S Supporting Information

ABSTRACT: The heavy atom effect on the magnetic anisotropy of septet trinitrenes is reported. Septet 1-bromo-3,5-dichloro-2,4,6-trinitrenobenzene (S-1) was generated in a solid argon matrix by ultraviolet irradiation of 1,3,5-triazido-2-bromo-4,6-dichlorobenzene. This trinitrene displays an electron spin resonance (ESR) spectrum that drastically differs from ESR spectra of all previously studied septet trinitrenes. The zero-field splitting (ZFS) parameters, derived from the experimental spectrum, show the parameter $|D| = 0.1237 \text{ cm}^{-1}$ and the unprecedentedly large ratio of $E/D = 0.262$ that is close to the rhombic limit $E/D = 1/3$ for high-spin molecules. The CASCI (based on state-averaged CASSCF) and DFT methods were applied to calculate the ZFS tensor focusing on the heavy (bromine) atom effects on the spin-orbit term. These calculations show that the multiconfigurational ab initio formalism and the CASCI method are the most successful for accurate predictions of the spin-orbit term in the ZFS tensor of high-spin nitrenes containing heavy bromine atoms. Due to the presence of the bromine atom in S-1, the contribution of the spin-orbit term to the total parameter D is dominant and responsible for the unusual orientation of the easy Z-axis lying in the molecular plane perpendicular to the C–Br bond. As a result, the principal values D_{xx} , D_{yy} , and D_{zz} of the total tensor \hat{D}_{Tot} have such magnitudes and signs for which the ratio E/D is close to the rhombic limit, and the total parameter D is large in magnitude and positive in sign.

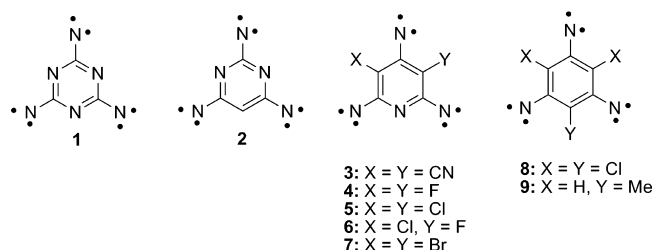


1. INTRODUCTION

High-spin nitrenes are highly reactive intermediates of the photolysis and thermolysis of aromatic polyazides, the spectral studies of which are possible only in cryogenic matrixes. These nitrenes have the largest zero-field splitting (ZFS) parameters D among all organic polyradicals and are of considerable interest as models for investigation of magnetism in molecular multispin systems.^{1,2} Because the ZFS parameters of high-spin nitrenes strongly depend on spin densities on the nitrene units, the mutual orientation of these units, and the type of atoms in molecules, the studies of such nitrenes provide an unique opportunity to examine in detail the effect of subtle structural changes on magnetic characteristics of open-shell molecules.^{3–5} The first electron spin resonance (ESR) spectra of quintet and septet nitrenes stabilized in frozen organic solutions were reported more than 40 years ago.^{6,7} In the next 4 decades, dozens of various quintet dinitrenes and septet trinitrenes were investigated with X-band ESR spectroscopy in frozen organic solutions.^{1,8} Unfortunately, many of the high-spin nitrenes appeared to be very reactive toward the organic solution molecules and could not be characterized with X-band ESR spectroscopy.^{9–12} An important breakthrough in ESR studies of high-spin nitrenes took place only recently owing to the use of the matrix isolation of high-spin nitrenes in solid inert gases. Using this technique, such previously elusive septet trinitrenes

as 1–4, as well as many other high-spin nitrenes, were successfully stabilized in solid inert gases and characterized with X-band ESR spectroscopy (Scheme 1).^{13–22} Moreover, the use of the matrix-isolation technique made possible the registration of high-resolution X-band ESR spectra of high-spin nitrenes, which is of paramount importance in analysis of very complex spectra representing a superposition of ESR spectra of several

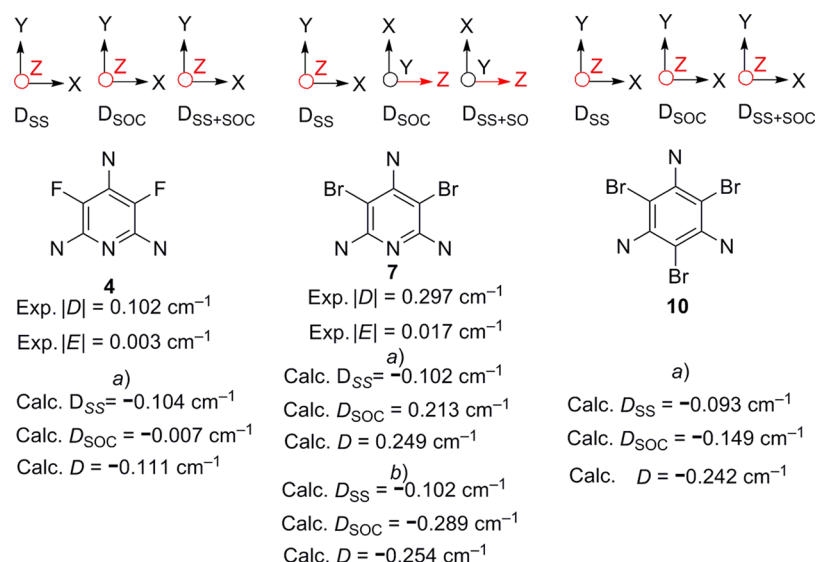
Scheme 1. Septet Trinitrenes Previously Studied in Solid Rare Gas Matrixes



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Scheme 2. ZFS Parameters of Previously Studied Septet Trinitrenes^a

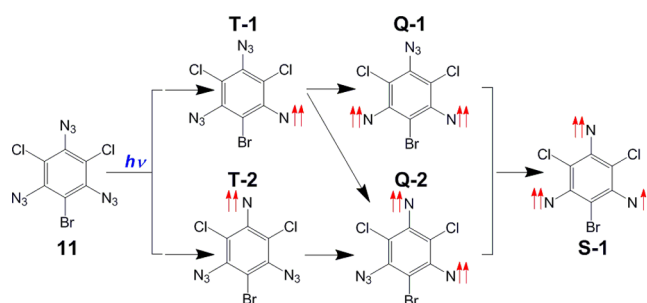
^aExperimental data from refs 13 and 19. Quantum chemical calculation data: (a) DFT, from refs 19 and 23; (b) ab initio (hybrid CASSCF/MRMP2), from ref 26.

high-spin species. Again, owing to chemical inertness of the solid rare gas matrixes, high-spin nitrenes isolated in these matrixes do not form molecular complexes with surrounding molecules, showing ESR spectroscopic characteristics identical to that estimated from quantum chemical calculations in the gas phase.^{5,17}

Extensive experimental^{13–22} and theoretical^{23–26} studies have shown that the dominant contribution to the parameter D of high-spin nitrenes containing light atoms arises from the dipolar spin–spin (SS) interactions, while the contribution of the anisotropic spin–orbit coupling (SOC) to the total parameter D is quite small (<10%). Among such trinitrenes, the largest negative value of $D = -0.123 \text{ cm}^{-1}$ was found for trinitrene **1**¹³ bearing the highest spin densities on the nitrene units. Other trinitrenes **2–6**, **8**, and **9** had lower spin densities on the nitrene units and, as a result, the lower negative values of D . Depending on the symmetry of the molecules, the E values of septet trinitrenes were either equal to zero (D_{3h} symmetric **1**, **8**, and **10**) or very small ($E/D \approx 0.04$, C_{2v} symmetric **2–6**). Such trinitrenes had the same orientations of the principal axes for the tensors \hat{D}_{SS} and \hat{D}_{SOC} (see trinitrene **4** in Scheme 2). The introduction of the heavy bromine atoms in septet trinitrenes considerably increased the contribution of the SOC part to the total parameter D (nitrenes **7** and **10**, Scheme 2), opening up the way to design of new promising organic magnetic molecules. In the case of D_{3h} symmetric trinitrene **10**, the orientations of the principal axes for the tensors \hat{D}_{SS} and \hat{D}_{SOC} were the same as those in trinitrenes **2–6**, **8**, and **9** (Scheme 2). By contrast, the Z -axis of the tensor \hat{D}_{SOC} in dibromine-substituted trinitrene **7** was directed along the line connecting two bromine atoms (Scheme 2). Due to the dominant contribution of the SOC part to the total parameter D of trinitrene **7**, the Z -axis of its total tensor \hat{D}_{Tot} coincided with the Z -axis of the tensor \hat{D}_{SOC} , thus essentially affecting the ZFS parameters of this trinitrene.

At the moment, all information about the effect of heavy atoms on the magnetic anisotropy of high-spin organic molecules is based only on the data of experimental studies of dibromine-substituted trinitrene **7**.¹⁹ Meanwhile, even a

small change in the number of bromine atoms may dramatically change the magnetic parameters of septet trinitrenes. To investigate these effects in detail, the photolysis of monobromine-substituted triazide **11** isolated in solid argon at 15 K was studied in the present work by using X-band ESR spectroscopy in combination with quantum chemical calculations (Scheme 3).

Scheme 3. Photolysis of Triazide **11**

2. METHODS

2.1. Experimental Section. Triazide **11** was synthesized by triazidation of commercially available 1-bromo-3,5-dichloro-2,4,6-trifluorobenzene (Sigma-Aldrich) according to a literature procedure.²⁷

The experimental technique for matrix isolation used in this study was similar to that described earlier.^{15,20} Solid argon films doped with triazide **11** were prepared by vacuum codeposition of two separate molecular beams (Ar and triazide **11** 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 **11** was produced by an oven heating the polycrystalline **11** to $\sim 87^\circ\text{C}$. The oven temperature was regulated by a precise temperature controller and was chosen to obtain the ratio Ar/triazide **11** of $\sim 10^3$ – 10^4 . Temperature stability was $\sim 0.1 \text{ K}$ over the 5–40 K range. ESR spectra were recorded using a

standard 9 GHz spectrometer (Radiopan; modulation frequency of 100 kHz) at sufficiently low microwave power to avoid the saturation effects. The modulation amplitude was low enough to avoid the line broadening. Photolysis of the samples was carried out at a temperature of 15 K by means of a Hg arc lamp (mercury spectral line lamp, Lot-Oriel) equipped with a narrow band filter at 254 nm.

2.2. Computational Methods. All quantum chemical calculations were performed with the ORCA program package (version 3.0.1).²⁸ The geometry of septet trinitrene **S-1** was optimized within the density functional theory at the B3LYP/TZVP level of theory. The equilibrium geometry configurations were confirmed by vibrational frequency calculations. The Cartesian coordinates of the optimized geometry of **S-1** and calculated vibrational frequencies are given in the Supporting Information. The magnetic parameters, including both the SS and the SOC, were obtained by the DFT method with the PBE²⁹ functional and the Ahlrichs-DZ³⁰ basis set. The contributions of the SS and SOC parts to the total \hat{D} tensor were calculated by using McWeeny–Mizuno^{31,32} and Peder–son–Khanna³³ approaches, respectively. In general, the PK-PBE/Ahlrichs-DZ approach gives a good agreement between experimental and calculated parameters of the \hat{D} tensors for high-spin nitrenes.²³

The ab initio values of the \hat{D} tensor (including both the SS and SOC parts) were obtained employing the CASCI method with 50 septet roots on the top of the state-averaged CASSCF wave function. This approach was successfully used previously for various high-spin molecules.^{34–36} The CASSCF active space consists of 12 orbitals and 12 electrons, as shown in Figure 1. According to Sugisaki and co-workers,²⁶ the correct active space for bromine-substituted nitrenes should include in-plane and out-of-plane lone pair orbitals of the valence p electrons of the bromine atoms (see the doubly occupied orbitals in Figure 1). The ab initio (CASCI) calculations of the ZFS parameters were performed with the SVP (Ahlrichs-VDZ)³⁰ electronic basis set. Preliminary test calculations revealed the absence of any noticeable influence of the basis set size on the accuracy of the ZFS calculations with both DFT and multiconfigurational approaches.³⁵

The total \hat{D} tensor was calculated by summation of the SS and SOC tensors, $\hat{D}_{\text{Tot}} = \hat{D}_{\text{SS}} + \hat{D}_{\text{SOC}}$. The conventional notations of the scalar ZFS parameters D and E are

$$D = \frac{3}{2}D_{ZZ} \quad E = \frac{D_{XX} - D_{YY}}{2} \quad (1)$$

where D_{XX} , D_{YY} , and D_{ZZ} are the eigenvalues of the traceless tensor \hat{D} . The “easy axis” Z is defined as $|D_{ZZ}| > |D_{XX}|, |D_{YY}|$. These conditions define the maximum ratio $|E/D| = 1/3$ if one of the eigenvalues equals zero. Subsequently, parameter D becomes ambiguous where E/D approaches the rhombic limit of $E/D = 1/3$.

3. RESULTS AND DISCUSSION

3.1. Powder ESR Spectra and ZFS Parameters. Brief UV irradiation (5 min) of triazide **11** at 15 K led to the appearance of the intense ESR line near zero magnetic field; see Figure 2a. Upon further irradiation, a number of additional ESR lines at 31, 65, 146, 173, 201, 241, 255, 267, 37, 348, 376, 470, and 513 mT appeared in the spectrum. The intensity of the strong ESR line at zero field reached its maximum value after ~20 min of irradiation time and then gradually decayed upon further irradiation. The intensities of the other ESR lines in the

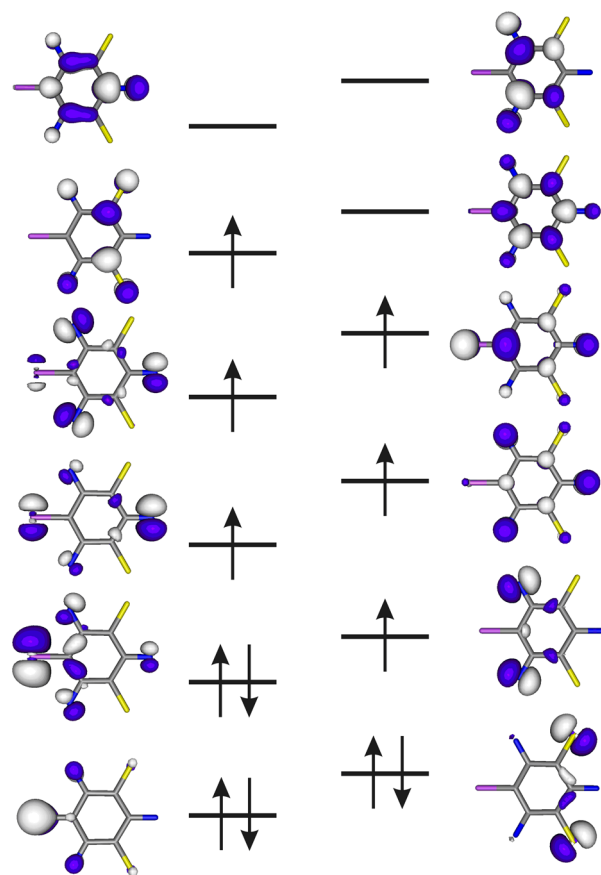


Figure 1. CASSCF active space and the orbital occupancies in the main configuration of septet trinitrene **S-1**.

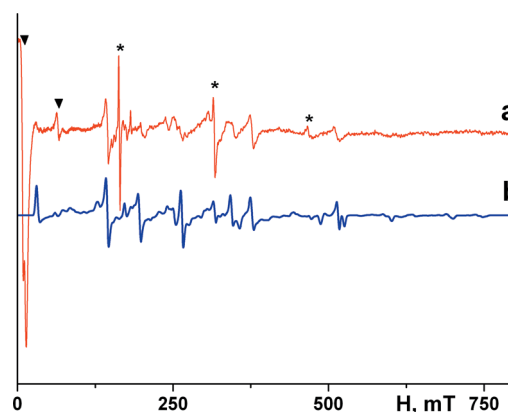


Figure 2. ESR spectra: (a) after 50 min of UV irradiation of triazide **11** in an argon matrix at 15 K; (b) simulation for **S-1** with $g = 2.003$, $D = 0.1237 \text{ cm}^{-1}$, and $E = 0.0324 \text{ cm}^{-1}$. Microwave frequency of 9.107 GHz. Two ESR lines assigned to quintet dinitrenes are marked with (▼). The ESR lines from impurities in the sapphire rod are marked with (*).

spectrum reached their maximum values after ~50 min of irradiation time.

Theoretically, the photolysis of triazide **11** should lead to the formation of triplet mononitrenes **T-1** and **T-2**, quintet dinitrenes **Q-1** and **Q-2**, and septet trinitrene **S-1** (Scheme 3). In our previous studies, the ESR spectra of triplet mononitrenes were observed as doublet ESR lines at 670–700 mT. Meanwhile, none of signals above 600 mT in the experimental spectrum in Figure 2a could be assigned to triplet

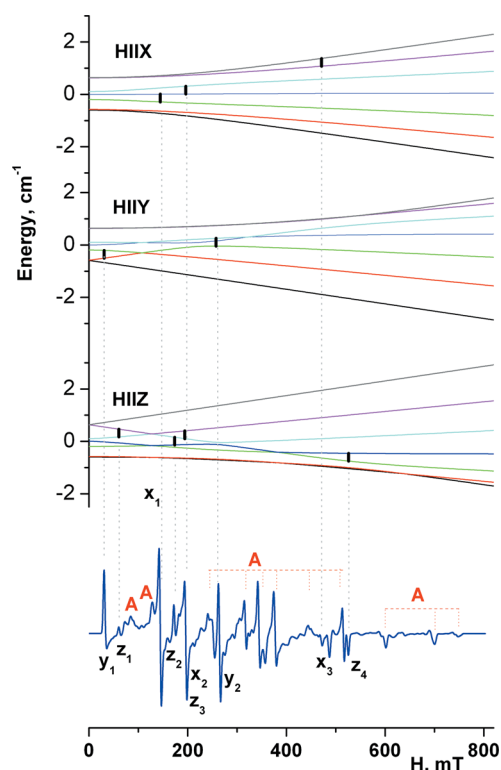


Figure 3. Zeeman energy levels and allowed transitions of septet trinitrene S-1 with $D = 0.1237 \text{ cm}^{-1}$ and $E = 0.0324 \text{ cm}^{-1}$.

mononitrenes T-1 and T-2. Apparently, these mononitrenes are photochemically very labile and readily photolyzed until quintet dinitrenes Q-1 and Q-2 and septet trinitrene S-1. Most quintet dinitrenes also demonstrate very poor spectra, consisting of two intense lines, one of them at low magnetic field (<100 mT) and another one near g_e (at ~300 mT). In contrast, all septet trinitrenes display a series of 5–7 intense lines at magnetic fields less than 400 mT. As a rule, one or two of these lines appear at very low magnetic fields (<100 mT) if the parameter $|D|$ is close to $\sim 0.1 \text{ cm}^{-1}$.

The line shape ESR spectral simulations were performed using the EasySpin program package,³⁷ operating with an exact numerical matrix diagonalization analysis of the spin Hamiltonian (eq 2) for randomly oriented molecules with total spin $S = 3$

$$\mathbf{H} = g\beta\mathbf{H}\mathbf{S} + \hat{\mathbf{S}}\mathbf{D}\mathbf{S} \quad (2)$$

The ZFS parameters of trinitrene S-1 were determined by comparison of the computer-simulated and experimentally recorded ESR spectra. This procedure was described in detail in refs 15 and 19. All of our attempts to simulate the lines at zero field and 65 mT for a septet spin state by tuning $|D|$ near its expected value of $0.1\text{--}0.3 \text{ cm}^{-1}$ were unsuccessful. On the other hand, a perfect agreement between the experiment and theory was achieved for $|D| = 0.1237 \text{ cm}^{-1}$ and $|E| = 0.0324 \text{ cm}^{-1}$. Figure 2 demonstrates that all intense ESR lines in the simulated spectrum reproduce all intense ESR lines in the experimental spectrum, except the lines at zero field and 65 mT. The last two lines in the experimental spectrum should be attributed to quintet dinitrenes Q-1 and Q-2. The tentative ZFS parameters of these dinitrenes and their simulated spectra are given in the Supporting Information.

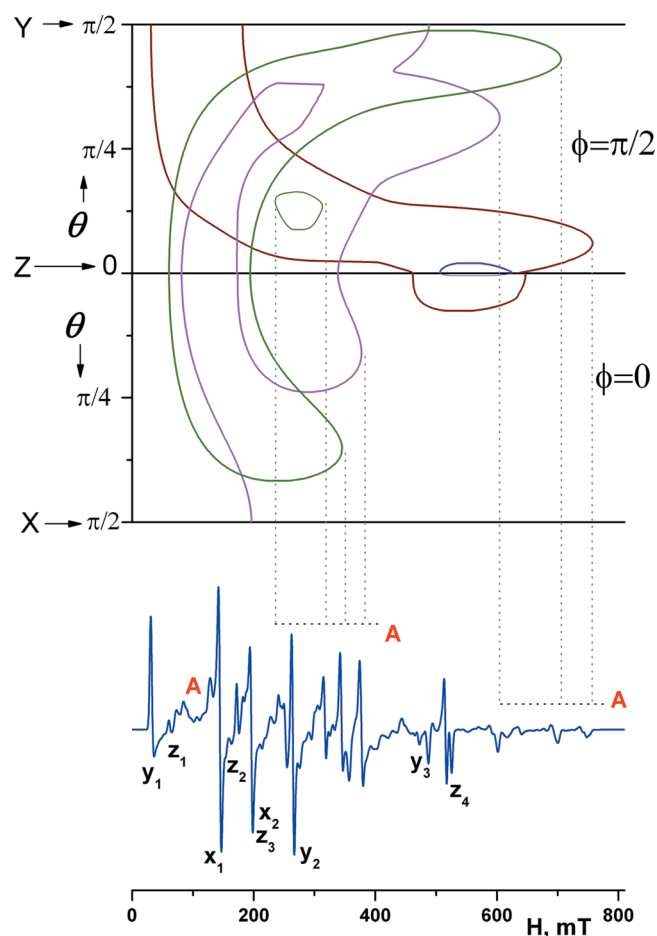


Figure 4. Angular dependences of resonance magnetic fields from the Euler angle θ for septet trinitrene S-1 with $D = 0.1237 \text{ cm}^{-1}$ and $E = 0.0324 \text{ cm}^{-1}$. Extra lines are marked as A.

Table 1. Experimental and Calculated ZFS Parameters D/cm^{-1} and E/D of Trinitrene S-1

parameter	Quantum Chemical Calculations		expt.
	UDFT (PK-PBE/Ahlrichs-DZ)	ab initio (CASCI(12,12)/SVP)	
D_{SS}	−0.094	−0.099	
D_{SOC}	0.131	−0.164	
D_{Tot}^a	0.177	0.123	0.124
$(E/D)_{\text{Tot}}$	0.18	0.260	0.262

^aThe Z principal axis of the tensor \hat{D}_{SS} does not coincide with that of the tensor \hat{D}_{SOC} ; see below.

To perform a complete and unambiguous assignment of all observable lines in the ESR spectrum of trinitrene S-1, the Zeeman energy levels for the canonical orientations (H||X, H||Y, and H||Z) and the angular dependences of resonance magnetic fields from the Euler angle θ were calculated based on the exact numerical solution of the spin Hamiltonian (eq 2) (Figures 3 and 4). These calculations show that the most intense lines in the spectrum of trinitrene S-1 are assigned to the perpendicular X- and Y-transitions at 31 (Y_1), 146 (X_1), and 201 (X_2) mT. Additionally, a series of intense “extra lines” (marked as A in Figures 3 and 4) appear in the spectrum from the molecules with off-principal-axis orientations. These extra lines appear in the powder EPR spectrum if $(d\theta/dH^{\text{res}})$ in Figure 4 is turned to infinity. Note that the experimental data

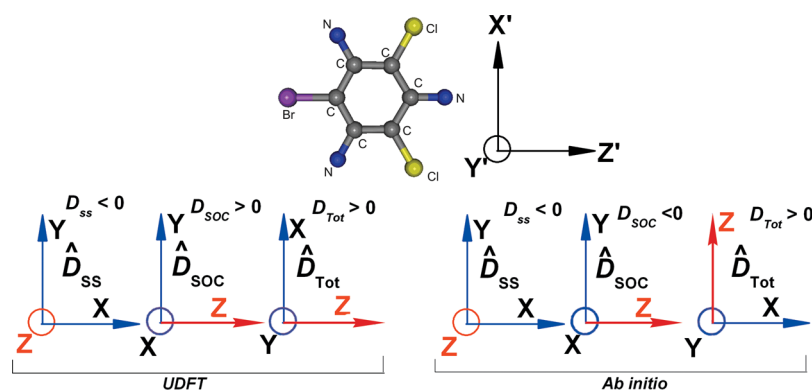


Figure 5. Principal axes of the tensors \hat{D}_{SS} , \hat{D}_{SOC} , and \hat{D}_{Tot} for septet trinitrene S-1 according to DFT and ab initio (CASCI) calculations.

Table 2. Principal Values of the Tensors \hat{D}_{SS} , \hat{D}_{SOC} , and \hat{D}_{Tot} for Septet Trinitrene S-1 in the Coordinate System Fixed to the Molecular Axes ($X'Y'Z'$; see Figure 5)^a

tensor	Calculations/cm ⁻¹					
	DFT			ab initio		
	$D_{X'X'}$	$D_{Y'Y'}$	$D_{Z'Z'}$	$D_{X'X'}$	$D_{Y'Y'}$	$D_{Z'Z'}$
\hat{D}_{SS}	0.0314	-0.0624^a	0.0310	0.0298	-0.0663	0.0365
\hat{D}_{SOC}	-0.0587	-0.0284	0.0871	0.0524	0.0570	-0.1094
\hat{D}_{Tot}	-0.0273	-0.0908	0.1181	0.0822	-0.0093	-0.0729

^aValues in boldface are the D_{ZZ} principal values in the conventional definition; see eq 1. The anisotropic (traceless) component of the tensor \hat{D}_{SOC} is shown.

obtained in the present work do not provide direct information about the sign of the parameter D . The Zeeman energy levels in Figure 3 were calculated for the positive D value. In the case of the negative D , the Zeeman energy levels just invert without changing the resonance fields and line intensities for all transitions even at a temperature of 5 K.

The ESR spectrum of trinitrene S-1 drastically differs from ESR spectra of all previously studied trinitrenes 1–9. Upon comparison with trinitrene 1 showing $|D| = 0.123 \text{ cm}^{-1}$, trinitrene S-1 with $|D| = 0.1237 \text{ cm}^{-1}$ is characterized by an unprecedentedly large ratio of $E/D = 0.262$ that is close to the rhombic limit $E/D = 1/3$ for high-spin molecules. Another effect of the bromine atom on the ZFS of septet trinitrenes is manifested in a large value of D of trinitrene S-1, exceeding in magnitude the D value of trinitrene 8 by 30%. To rationalize all of these effects in septet trinitrenes, extensive quantum chemical calculations were carried out.

3.2. Quantum Chemical Calculations of the ZFS Parameters. Previous DFT and ab initio studies showed that the magnitude and the sign of the total parameter D depend on the SOC term in bromine-containing high-spin nitrenes.^{19,26} Unfortunately, X-band ESR spectroscopy does not provide direct information about the sign of the parameter D in high-spin molecules. Therefore, to estimate the performance of our quantum chemical calculations, we used the experimental parameter $|D| = 0.1237 \text{ cm}^{-1}$ and the ratio $E/D = 0.262$ of trinitrene S-1 as two references. Because previous DFT¹⁹ and ab initio (hybrid CASSCF/MRMP2)²⁶ calculations gave different signs of the parameter D for dibromine-substituted trinitrene 7, we paid special attention in our calculations to the sign of D and to its formation under comparable magnitudes of anisotropic SS and SOC interactions. The results of calculations are summarized in Table 1. Both quantum chemical approaches predict the positive sign of the total parameter D_{Tot} . The UDFT calculations significantly overestimate the magnitude of D and

underestimates the ratio E/D for trinitrene S-1. By contrast, the CASCI(12,12)/SVP calculations demonstrate excellent agreement with the experimental data. The analysis of the SS and SOC parts of the tensor \hat{D} shows that both methods predict essentially the same negative parameters D_{SS} representing typical values for most of the septet trinitrenes. On the other hand, these methods predict different magnitudes and opposite signs for the parameters D_{SOC} .

An answer to the question of why both theoretical methods predict a positive sign of the total parameter D_{Tot} for trinitrene S-1 can be obtained from analysis of the principal axes and principal values of the D tensors of this trinitrene (see Figure 5 and Table 2).

Both DFT and ab initio calculations predict that the Z -axis (easy axis) of the tensor \hat{D}_{SS} is perpendicular to the molecular plane, while the Z -axis of the tensor \hat{D}_{SOC} lies in a molecular plane and is directed along the C–Br bond. Because the Z -axes of the tensors \hat{D}_{SS} and \hat{D}_{SOC} do not coincide, the total parameter D_{Tot} is not a simple scalar sum of D_{SS} and D_{SOC} . The ab initio calculations show that summation of the principal values $D_{X'X'}$, $D_{Y'Y'}$, and $D_{Z'Z'}$ of the tensors \hat{D}_{SS} and \hat{D}_{SOC} in the coordinate system fixed to the molecular axes (see Table 2) gives the highest magnitude of $D_{X'X'}$ in the total tensor \hat{D}_{Tot} , thus predicting the positive sign of D_{Tot} . Subsequently, the easy axis of \hat{D}_{Tot} corresponds to the X' -axis lying in the molecular plane perpendicular to the C–Br bond (Figure 5). Due to a small difference in magnitudes of the $D_{X'X'}$ and $D_{Z'Z'}$ components, the ratio E/D for trinitrene S-1 is close to the rhombic limit. In contrast, the DFT calculations give the highest magnitude of $D_{Z'Z'}$ in the total tensor \hat{D}_{Tot} and opposite sign for the parameters D_{SOC} . Nevertheless, these calculations also predict the positive sign of D_{Tot} for trinitrene S-1.

4. CONCLUSIONS

As in the case of bromine-containing trinitrenes **7** and **10**, the contribution of the SOC term to the total parameter D of septet trinitrene **S-1** substantially exceeds the contribution of the SS term. However, in the case of trinitrene **S-1**, the easy Z -axis of the magnetic system lies in the molecular plane. As a result, the principal values $D_{XX'}$, $D_{YY'}$, and $D_{ZZ'}$ of the total tensor \hat{D}_{Tot} have such magnitudes and signs for which the ratio E/D is close to the rhombic limit and the total parameter D is large in magnitude and positive in sign. Due to these effects, the X-band ESR spectrum of trinitrene **S-1** with $|D| = 0.1237 \text{ cm}^{-1}$, and $E/D = 0.262$ drastically differs from ESR spectra of all previously studied septet trinitrenes. The experimental ZFS parameters of **S-1** are reproduced well by the CASCI(12,12)/SVP calculations. In comparison with these calculations, DFT calculations are much less precise, especially in predictions of the SOC term. According to recent studies,²⁶ the problems of DFT-based theoretical approaches in estimations of the SOC terms of the bromine-containing nitrenes arise due to the strong delocalization of the singly occupied molecular orbitals of such molecules onto the bromine atoms.

■ ASSOCIATED CONTENT

Supporting Information

(1) Cartesian coordinates of the optimized geometry of trinitrene **S-1**. (2) Tentative ZFS parameters of dinitrenes **Q-1** and **Q-2**. (3) Calculated vibrational frequencies of trinitrene **S-1**. 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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