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Strain Effects in Electron Spin Resonance Spectroscopy of Quintet 2,6-Bis(4'-nitrenophenyl)-4-phenylpyridine

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 Supporting Information

ABSTRACT: Photolysis of 2,6-bis(4'-azidophenyl)-4-phenylpyridine in 2-methyltetrahydrofuran (2MTHF) glass at 7 K leads to quintet 2,6-bis(4'-nitrenophenyl)-4-phenylpyridine as a mixture of rotational isomers. The electron spin resonance (ESR) spectrum of this mixture of rotamers shows a considerable broadening of many transitions in the range of 0–5000 G and cannot be reproduced by computer simulations solely based on the tuning of the spin Hamiltonian parameters g , D_Q , and E_Q alone or on predictions of DFT calculations. The best modeling of the experimental ESR spectrum is obtained only when the large line-broadening parameter of $\Gamma(E_Q) = 1200$ MHz along with the spin Hamiltonian $g = 2.003$, $D_Q = 0.154$ cm⁻¹, and $E_Q = 0.050$ cm⁻¹ is used in the spectral simulations. The most accurate theoretical estimations of the magnetic parameters of the dinitrene in a 2MTHF glass are obtained from the B3LYP/6-311+G(d,p)+PBE/DZ/COSMO calculations of the spin–spin coupling parameters D_{SS} and E_{SS} . Such calculations overestimate the E_Q and D_Q values of the dinitrene just by 1% and 10%, respectively, demonstrating that contributions of the spin–orbit coupling parameters D_{SOC} and E_{SOC} to the total D_Q and E_Q values are negligibly small. The research shows that ESR studies of polynuclear high-spin nitrenes, obtained by photolysis of rotational isomers of the starting azides, can only be successful if large E_Q strain effects are taken into account in the spectral simulations.



INTRODUCTION

High-spin nitrenes are of considerable interest as models for magneto-structural studies of open-shell multispin molecular systems. The magnetic parameters of such nitrenes strongly depend on spin densities on the nitrene units and the mutual orientation of these units, thus providing an opportunity to examine in detail the effect of subtle structural changes on magnetic properties of high-spin molecular clusters.^{1–5} Moreover, after development of modern quantum-chemical programs⁶ for calculation of zero-field splitting (ZFS) parameters in high-spin molecules, experimental studies of high-spin nitrenes are important for testing and further optimization of such programs. Thus far, most of the magneto-structural studies of quintet dinitrenes^{1–3} and septet trinitrenes^{4,5} were performed for relatively small molecules with rigid molecular structures (e.g., **1–10**). The random-orientation X-band ESR spectra of such nitrenes in various types of cryogenic matrices (2MTHF glass, solid argon, host crystals) could readily be reproduced by simulations based on the tuning of the spin Hamiltonian parameters g , D , and E . A very good agreement was found for high-spin nitrenes such as **9** or **10** matrix isolated in argon.^{5a,e} Unfortunately, matrix isolation is limited to small precursor molecules that can be sublimed without decomposition. The most general method to investigate high-spin nitrenes is powder ESR spectroscopy in organic rigid

glasses.^{1,2,4,7,8} Due to the anisotropic solvation of high-spin nitrenes in organic glasses, the zfs parameters D and E derived from such spectra can dramatically differ from those measured in rare gases or predicted by DFT calculations.^{5d} However, even in these cases computer simulations can adequately reproduce the random-orientation ESR spectra of high-spin nitrenes with a rigid molecular structure.^{1,2,4}

A different situation is observed for dinitrenes with a flexible molecular structure (e.g., **11–16**).^{7,8} ESR spectra of these flexible dinitrenes have not been reliably simulated so far. Only for dinitrene **16** magnetic parameters of $D_Q = 0.2009$ cm⁻¹ and $E_Q = 0.0358$ cm⁻¹ were reported.⁸ However, since D_Q values of quintet dinitrenes with a meta orientation of the nitrene units at the aromatic ring should be at least five times smaller than the $D_T = 0.929$ cm⁻¹ of the parent triplet azidonitrene,³ the reported D_Q of **16** seems to be unrealistically large.

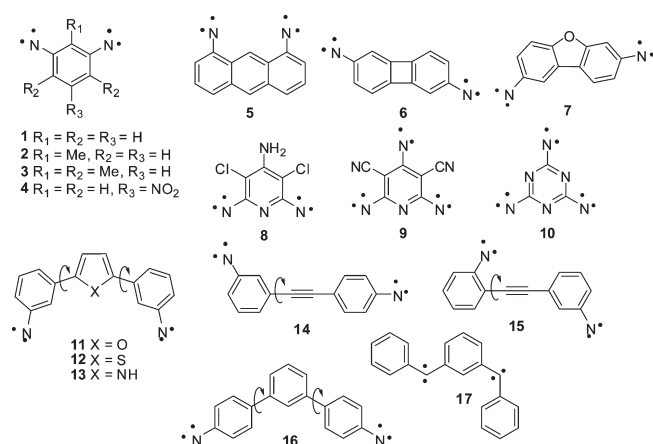
The uncertainty in the analysis of ESR spectra of the flexible dinitrenes **11–16** is mainly caused by a considerable broadening of many ESR signals resulting from numerous rotational isomers with slightly different D_Q and E_Q . A typical example showing the

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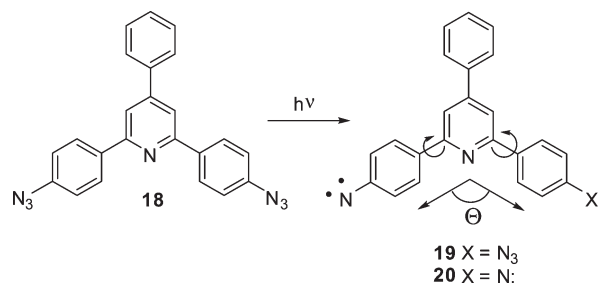
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influence of these strain effects on the ESR spectrum is quintet dicarbene **17**. The X-band ESR spectrum of **17** in 2MTHF glass



could be reproduced by computer simulations only recently after introducing large line-broadening parameters $\Gamma(D_Q)$ and $\Gamma(E_Q)$ in addition to the spin Hamiltonian parameters g , D_Q and E_Q . Due to this broadening, the ESR spectra of flexible dinitrenes can adopt unusual line shapes such that even approximate estimation of their magnetic parameters from simulations becomes very problematic.

Here, we report investigations of strain effects on the ESR spectrum of quintet dinitrene **20**, composed of numerous rotational isomers with slightly different values of D_Q and E_Q . The ESR spectrum of quintet dinitrene **20** formed during photolysis of diazide **18** in 2MTHF glass at 7 K has been analyzed by using extensive computer simulations in combination with DFT calculations.



EXPERIMENTAL SECTION

Diazide **18** was synthesized according to a literature procedure.¹⁰

X-band ESR spectra were recorded with a Bruker-Elexsys E500 ESR spectrometer with an ER077R magnet (75 mm gap between pole faces), an ER047 XG-T microwave bridge, and an ER4102ST resonator with a TE₁₀₂ cavity. 2-Methyltetrahydrofuran (2MTHF) glass doped with diazide **18** was prepared by cooling a 4 mm o.d. quartz sample tube containing a degassed solution of **18** in 2MTHF (diazide concentration of ca. 10^{-4} M) in the cavity of the ESR spectrometer to 7 K. The matrix-isolated sample was 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 ESR spectra were performed by using the EasySpin program package (version 3.1.0)¹¹ for $S = 1$ and 2 using the parameters $\nu = 9.4782$ GHz, $g = 2.003$, and line broadening parameters $\Gamma(D_Q)$ and $\Gamma(E_Q)$ in the 0–2000 MHz

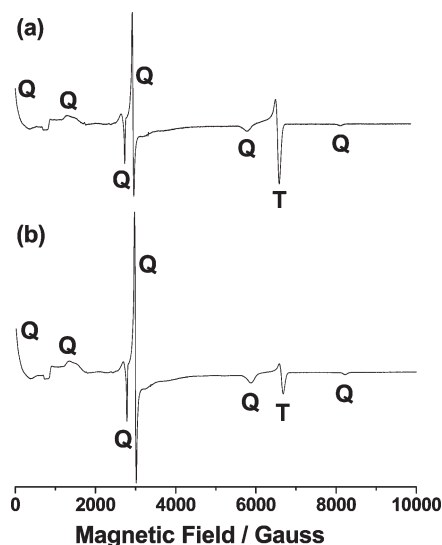


Figure 1. EPR spectra (a) after 3 min and (b) after 33 min of irradiation of diazide **18** in 2MTHF glass at 7 K.

region. The accuracy of the D_Q and E_Q parameters determination was <0.001 and 0.0005 cm⁻¹, respectively. The EasySpin program package was also used for the eigenfield calculations of the Zeeman energy levels for canonical orientations of the tensor D_Q ($H||X$, $H||Y$, $H||Z$).

Density functional theory (DFT) calculations were performed with the Gaussian 03 program package.¹² The geometries of the molecules were optimized by using the B3LYP functional¹³ in combination with the 6-311+G** basis set. The nature of the stationary points was assessed by means of vibrational frequency analysis. The spin Hamiltonian parameters g , D_Q , and E_Q were obtained from additional single-point calculations with the ORCA program package (Version 2.8.0.1)⁶ by using for this purpose the PBE functional in combination with the DZ basis set. The ORCA program package was also used for calculations of the direct spin–spin (SS) coupling and spin–orbit coupling (SOC) parts of the quintet tensor D_Q by using the unrestricted Pederson–Khanna¹⁴ approach. To investigate the influence of the 2MTHF matrix on magnetic parameters of dinitrene **20**, the conductor-like screening model (COSMO),¹⁵ implemented into the ORCA program, was used. Within this model, the continuum is initially assumed to be a perfect conductor that completely screens the charge density of the solute. After determination of the screening charges, they were scaled down to a finite dielectric constant $\epsilon = 7.0$ of 2MTHF and implemented to the Hamiltonian of the system. The screening charges were calculated for realistic, van der Waals like, molecular cavities.

RESULTS AND DISCUSSION

Brief irradiation (3 min, $\lambda > 305$ nm) of diazide **18** in 2MTHF glass at 7 K led to the appearance of the characteristic ESR X_2Y_2 transition of triplet nitrene **19** at 6630 G and a series of transitions at 30, 900, 1350, 2765, 2995 (most intense), 5880, and 8224 G that can be assigned to quintet dinitrene **20** (Figure 1a). On further irradiation, the intensity of the ESR signal of the triplet nitrene gradually decreases while the intensities of the ESR signals of the quintet dinitrene reach their maxima (Figure 1b). These spectral changes suggest that diazide **18** undergoes a stepwise photochemical decomposition of the azido groups to

Table 1. Calculated and Experimentally Determined Spin Hamiltonian Parameters of Quintet Dinitrene 20

data	nitrene	method	g factor	D/D_{SS} (cm^{-1})	E/E_{SS} (cm^{-1})
PBE/DZ calculations	20- <i>anti</i> -I	conventional	2.0036	0.1871/0.1764	0.0555/0.0521
		COSMO	2.0036	0.1814/0.1709	0.0539/0.0506
	20- <i>anti</i> -II	conventional	2.0036	0.1867/0.1760	0.0554/0.0520
		COSMO	2.0036	0.1828/0.1722	0.0540/0.0507
	20- <i>syn</i>	conventional	2.0036	0.1859/0.1752	0.0551/0.0517
		COSMO	2.0036	0.1742/0.1714	0.0512/0.0503
experiment	20	ESR	2.0030	0.1540	0.050

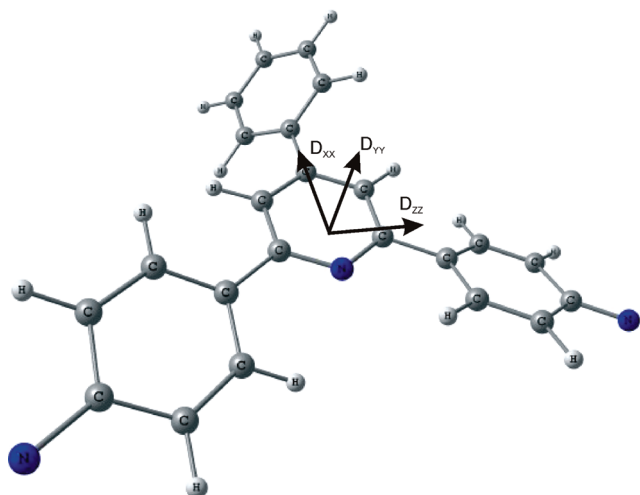


Figure 2. B3LYP/6-311+G(d,p)-optimized molecular structure and PBE/DZ-calculated orientation of the tensor D_Q of *anti*-I isomer of quintet dinitrene 20.

form triplet nitrene **19** and subsequently quintet dinitrene **20**. For the triplet nitrene **19** the magnetic parameters $g = 2.003$, $D_T = 0.91 \text{ cm}^{-1}$, and $E_T = 0 \text{ cm}^{-1}$ were determined from simulations of the spectra. The D_T value of 0.91 cm^{-1} is typical for triplet nitrenes with an extended aromatic system. Thus, for instance, triplet 3'-(4'-azidophenyl)-4-biphenylnitrene, a precursor of quintet dinitrene **16**, shows a D_T value of 0.929 cm^{-1} in 2MTHF glass at 3 K.⁸

At first glance the ESR spectrum of quintet dinitrene **20** resembles the spectra of other quintet dinitrenes with meta orientation of the nitrene units in the aromatic ring, such as dinitrene **14**.^{7a} The dipolar angle Θ between the nitrene C–N bonds in most of these dinitrenes is in the range of 117 – 125° , which results in a ratio $|E_Q/D_Q|$ of approximately 0.2 (eq 1).³

$$|E_Q/D_Q| \approx [\cos^2(\Theta/2)]/[2 - 3\cos^2(\Theta/2)] \quad (1)$$

The fine structure (FS) spectra of these dinitrenes are usually characterized by weak and broad Z_1 , Z_2 , X_1 , and Y_1 transitions in the 500–1600 G region, a weak X_2 transition at ~ 2700 G, the most intense Y_2 transition at ~ 3000 G, and six canonical X_3 , X_4 , Y_3 , Y_4 , Z_3 , and Z_4 transitions along with three off-principal-axis transitions in the 3000–10 000 G region.² The off-principal-axis transition at 5800–6300 G and the canonical X_4 transition at 8000–8400 G are the most characteristic features in the spectra. Extensive spectral simulations showed that the position of the most intense transition at ~ 3000 G is determined by a particular combination of the D_Q and E_Q values, the resonance field of the

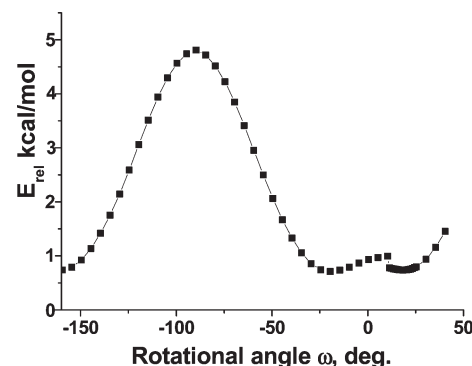


Figure 3. Calculated (B3LYP/6-311+G(d,p)) energy as a function of the fixed torsional angle ω of one of the nitrenophenyl rings in quintet dinitrene **20**. The torsional angles of the other two phenyl rings are optimized to minimize the energy.

off-principal-axis transition at 5800–6300 G depends exclusively on D_Q and the position of the canonical X_4 transition at 8000–8400 G mostly depends on E_Q . However, none of the EPR spectra simulated for a quintet spin state with $g = 2.003$ and $E_Q/D_Q = 0.038/0.192$, $0.039/0.188$, $0.040/0.184$, $0.041/0.180$, $0.042/0.176$, $0.043/0.172$, or $0.044/0.168$ matched the experimental spectrum of dinitrene **20** satisfactorily, although all the simulated spectra precisely reproduced the resonance field of the major transition at 2995 G (examples of these spectra are given in the Supporting Information).

In order to estimate the magnetic parameters of dinitrene **20**, single-point PBE/DZ calculations of the spin Hamiltonian parameters g , D_Q , and E_Q were performed on the UB3LYP/6-311+G(d,p) geometry. Recent studies suggest that deviations of D_Q and E_Q of quintet dinitrenes calculated at the PBE/DZ level of theory from the experimental values are about 10% (Table 1).¹⁶

The most stable structure of dinitrene **20** shows both phenyl rings being twisted from the plane of the pyridine ring by -19.8° and $+19.8^\circ$ (*anti*-I isomer, Figure 2).¹⁷ The angles between the principle magnetic axes D_x , D_y , and D_z (angle Θ) of the two individual triplet nitrene subunits in this rotational isomer are 33.4° , 33.4° , and 111.8° , respectively. In accordance with theory,³ the resulting D_{ZZ} axis is connecting the two triplet nitrene units and the D_{XX} axis lies in the plane of the pyridine ring. Rotation of the phenyl rings relative to the pyridine ring up to 30° in both directions results in a large number of energetically almost degenerate conformers of **20**. Thus, the frozen 2MTHF solution formed after photolysis of diazide **18** most likely consists of a broad distribution of conformers of **20** (Figure 3). The conformers that are formed on rotating the phenyl rings relative to

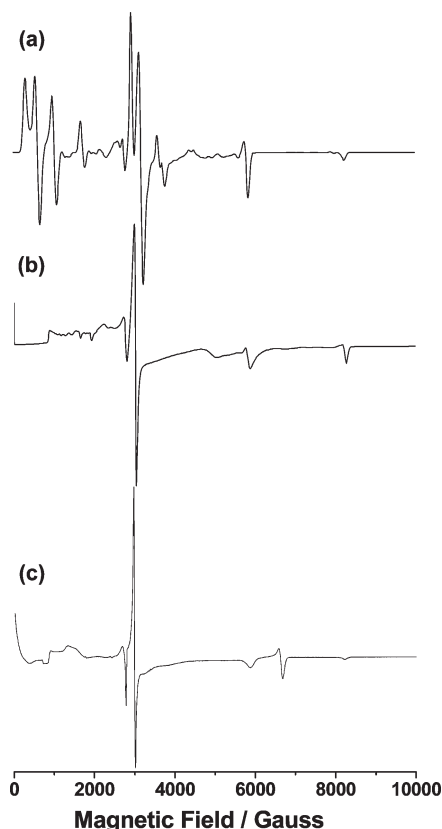


Figure 4. EPR spectra: (a) simulated spectrum for quintet molecules with $g = 2.003$, $D_Q = 0.154 \text{ cm}^{-1}$, and $E_Q = 0.050 \text{ cm}^{-1}$; (c) simulated spectrum for quintet molecules with $g = 2.003$, $D_Q = 0.154 \text{ cm}^{-1}$, $E_Q = 0.050 \text{ cm}^{-1}$, and $\Gamma(E_Q) = 430 \text{ G}$; (d) experimental spectrum (MWF = 9.4782 GHz) after 33 min of UV irradiation of diazide **18** in 2MTHF glass at 7 K.

the pyridine ring clockwise by 19.8° (*anti*-I isomer **20**) or counterclockwise by 20° (*anti*-II isomer **20**), respectively, are minima. The syn isomer **20** formed by rotating one phenyl ring clockwise and the other ring counterclockwise by 10° is calculated to be only 300 cal/mol higher in energy than the *anti*-I and *anti*-II isomers of **20** (see Supporting Information). According to PBE/DZ calculations, these three rotational isomers show nearly the same D_Q and E_Q values (Table 1). Since the angle Θ in the rotamers is close to 111.8° , their FS spectra are described by the same ratio $E_Q/D_Q = 0.297$. The total D_Q and E_Q values can be broken down into two components each: D_{SS} and E_{SS} that characterize the direct spin–spin dipole–dipole coupling and D_{SOC} and E_{SOC} characterizing the spin–orbit coupling. As expected for organic high-spin nitrenes, the contributions of D_{SOC} and E_{SOC} to D_Q and E_Q are very small for dinitrene **20** (approximately 6%).¹⁶ The small contributions of the spin–orbit interactions to the magnetic parameters is also reflected by the calculated g factor of 2.0036, which is only slightly larger than g for the free electron (2.0023). These conclusions are in good agreement with recent quantum-chemical calculations (CASSCF/MRMP2),¹⁸ showing that the contributions of D_{SOC} and E_{SOC} to the total D and E values of nitrenes do not exceed 11%.

The ESR spectrum of dinitrene **20** simulated with the PBE/DZ-calculated spin Hamiltonian parameters g , D_Q , E_Q , D_{SS} , and E_{SS} did not match the experimental ESR spectrum satisfactorily (see Supporting Information). In the simulated spectrum the two

characteristic high-field transitions of the quintet spin state at 5880 and 8224 G were strongly shifted to higher field, indicating a considerable overestimation of the parameters D_Q and D_{SS} in the simulation. At the same time, these simulations reproduced the difference of 2340 G between the two high-field transitions, indicating that the calculated ratio $E_Q/D_Q = 0.297$ is quite close to the experimental ratio. According to theory,³ quintet dinitrenes with E_Q/D_Q ratios in the range between 0.30 and 0.33 should show D_Q values that are equal to approximately $1/6 D_T$ of the parent triplet mononitrene. Since triplet mononitrene **19** shows a D_T value of 0.91 cm^{-1} , D_Q of dinitrene **20** should be about $0.152\text{--}0.154 \text{ cm}^{-1}$. Moreover, previous studies have shown that ESR spectra of quintet dinitrenes with $\Theta \approx 112^\circ$ recorded in 2MTHF glass are described by $E_Q/D_Q \approx 0.33$.^{2e} From that we estimate E_Q for dinitrene **20** in the range between 0.050 and 0.051 cm^{-1} . Indeed, spectral simulations for a quintet spin state with $g = 2.003$, $D_Q = 0.154 \text{ cm}^{-1}$, and $E_Q = 0.050 \text{ cm}^{-1}$ precisely reproduced the resonance fields of the two characteristic high-field transitions at 5880 and 8224 G (Figure 4a). However, transitions below 4000 G in the spectrum simulated with these parameters drastically differ from those observed in the experimental spectrum. Several factors such as g strain, D_Q strain, E_Q strain, or ordering effects could be responsible for these unusual FS patterns in the experimental X-band ESR spectra.⁹ Attempts to improve the simulated spectrum (Figure 4a) by variation of the line-broadening parameters $\Gamma(g)$, $\Gamma(D_Q)$, or ordering parameters were unsuccessful. On the other hand, the use of a line-broadening parameter $\Gamma(E_Q)$ of 1200 MHz ($\sim 430 \text{ G}$ or 0.04 cm^{-1}) in combination with the spin Hamiltonian parameters $g = 2.003$, $D_Q = 0.154 \text{ cm}^{-1}$, and $E_Q = 0.050 \text{ cm}^{-1}$ allowed us to successfully simulate the experimental spectrum of dinitrene **20** (Figure 4b). The large E_Q strain effect found indicates the existence of numerous rotamers of **20** in the frozen 2MTHF solution with slightly differing parameters D_Q and E_Q . According to theory,^{2e,3} both D_Q and E_Q values of quintet dinitrenes are functions of the dipolar angle Θ and the D_T value of the parent triplet mononitrene

$$D_Q \approx D_T [3 \sin^2(\Theta/2) - 1]/6 \quad (2)$$

$$E_Q \approx D_T [\cos^2(\Theta/2)]/6 \quad (3)$$

Thus, for instance, the ratio E_Q/D_Q of quintet dinitrene **20** varies from 0.297 to 0.305 even in the narrow range of $\Theta = 111.2\text{--}111.8^\circ$ (Figure 5).¹⁸ The angle Θ is, in turn, a function of the rotational angle ω (Figure 6).¹⁷ As a result, D_Q , E_Q , and E_Q/D_Q of quintet dinitrene **20** vary on changing the angle ω (Figures 7–9).¹⁷ Analysis of such changes shows that variations of D_Q and E_Q in the range of ω from -9 to -63° for dinitrene **20** reach 0.013 and 0.005 cm^{-1} , respectively. It should be noted that both $\Delta D_Q = 0.013 \text{ cm}^{-1}$ and $\Delta E_Q = 0.005 \text{ cm}^{-1}$ are calculated for dinitrene **20** in the gas phase. Recent studies^{9a} show that ESR spectra of even such structurally rigid molecules as quintet dinitrene **1** are noticeably distorted in 2MTHF glass. This is due to the E_Q strain effect caused either by specific solvent interactions between the dinitrene and 2MTHF or by steric interactions with the liberated nitrogen molecules in the rigid organic glass. In the structurally flexible **20** especially large E_Q strain effects are observed.

The comparison of experimental and calculated magnetic parameters D_{SS} and E_{SS} of quintet dinitrene **20** shows that

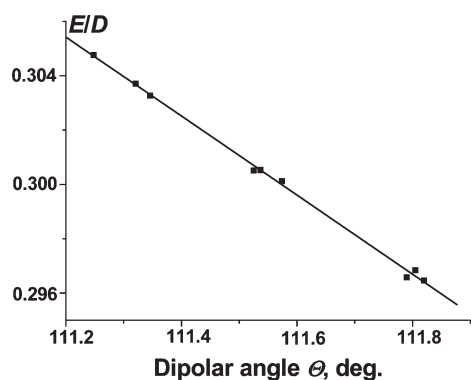


Figure 5. Dependence of the ratio E_Q/D_Q of quintet dinitrene **20** from the dipolar angle Θ . $R = 0.9989$.

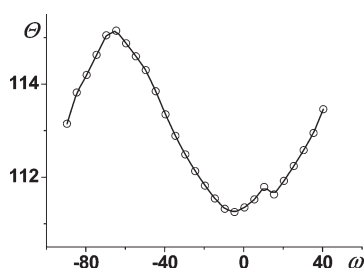


Figure 6. Calculated (B3LYP/6-311+G(d,p)) dipolar angle Θ as a function of the fixed torsional angle ω of one of the nitrenophenyl rings in quintet dinitrene **20**. The torsional angles of the other two phenyl rings are optimized to minimize the energy.

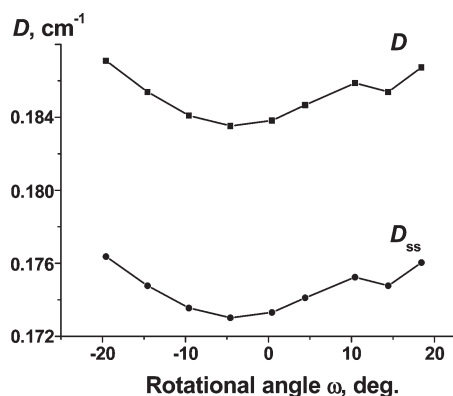


Figure 7. Calculated (PBE/DZ) parameters D and D_{SS} as a function of the fixed torsional angle ω of one of the nitrenophenyl rings in quintet dinitrene **20**. The torsional angles of the other two phenyl rings are optimized to minimize the energy.

PBE/DZ/COSMO calculations are most reliable (Table 1). At this level of theory the E_Q value of quintet dinitrene **20** is overestimated by only 1% while D_Q is by about 10%. It should be noted that the COSMO model is a typical continuum model that does not take into account specific interactions, such as hydrogen bonding between the molecules of the dinitrene and 2MTHF. These specific interactions might play a noticeable role, reducing the spin densities at the nitrene units and thus the D_Q values of high-spin nitrenes. Overall, the use of the COSMO model increases the accuracy of calculations of D_Q and E_Q of

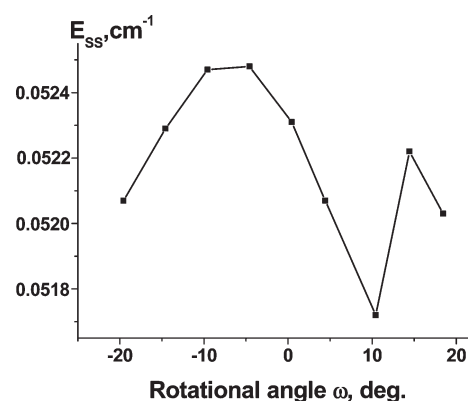


Figure 8. Calculated (PBE/DZ) parameter E_{SS} as a function of the fixed torsional angle ω of one of the nitrenophenyl rings in quintet dinitrene **20**. The torsional angles of the other two phenyl rings are optimized to minimize the energy.

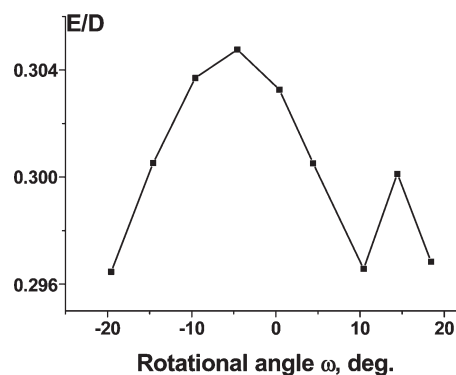


Figure 9. Calculated (PBE/DZ) ratio E_Q/D_Q as a function of the fixed torsional angle ω of one of the nitrenophenyl rings in quintet dinitrene **20**. The torsional angles of the other two phenyl rings are optimized to minimize the energy.

quintet dinitrenes by 6%. In organic dinitrenes the contributions of the D_{SOC} and E_{SOC} to the total D_Q and E_Q values are negligibly small and the magnetic parameters can be reliably estimated from PBE/DZ/COSMO calculations of the D_{SS} and E_{SS} values.

The ESR spectrum of **20** with two very strong signals around 3000 G drastically differs from ESR spectra of previously studied quintet dinitrenes (Figure 4a).^{1–3} In order to assign all transitions in this spectrum, the Zeeman energy levels for the canonical orientations ($H||X$, $H||Y$, $H||Z$) were calculated based on the exact numerical solution of the spin Hamiltonian for a quintet spin state with $g = 2.003$, $D_Q = 0.154$ cm⁻¹, and $E_Q = 0.050$ cm⁻¹. It was found that this quintet state gives only 10 transitions of high probability (3 X, 4 Y, and 3 Z, shown as solid lines in Figure 10), whereas 10 other transitions (5 X and 5 Z, shown as dotted lines in Figure 10) are forbidden and have at least 4 orders of magnitude lower probability. Besides these canonical transitions, the ESR spectrum also displays a set of signals at 290, 1690, 2765, 3150, and 5860 G assigned to off-principal-axis transitions arising from noncanonically oriented molecules of dinitrene **20** (marked with "A" in Figure 10).^{2,3} The quintet spin state with $g = 2.003$, $D_Q = 0.154$ cm⁻¹, and $E_Q = 0.050$ cm⁻¹ and its resulting ESR spectrum (Figure 4a) describe only one of the numerous rotamers of dinitrene **20**, presumably the *anti-I* isomer (Figure 2). In contrast, the

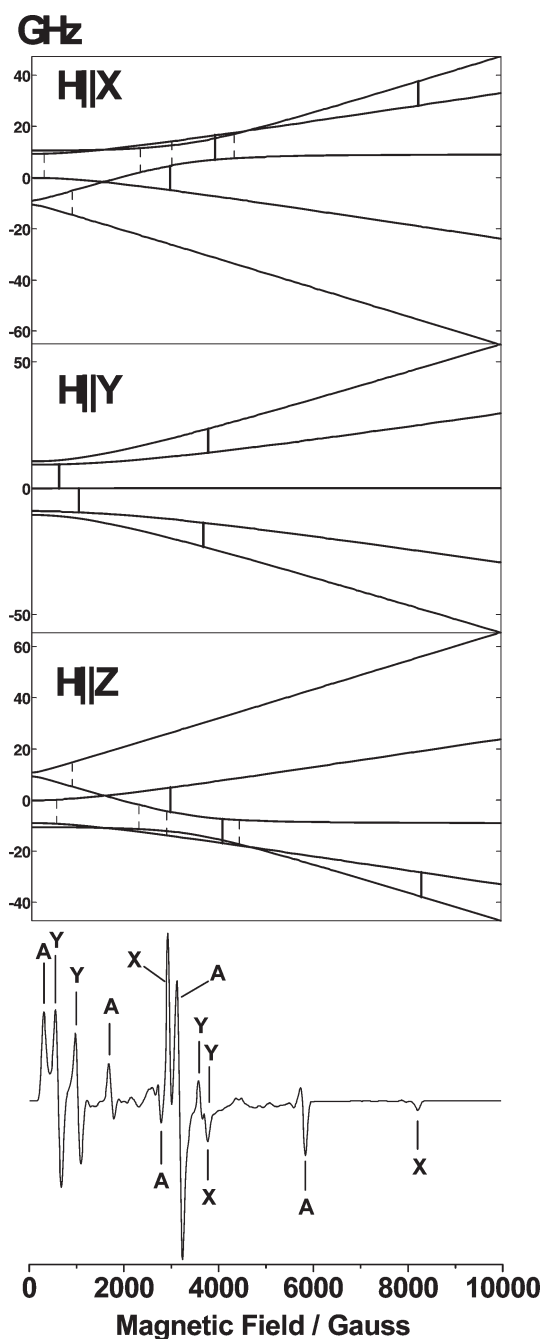


Figure 10. Zeeman levels and allowed transitions of quintet dinitrene **20**. “A” shows the extra lines from noncanonical transitions of dinitrene **20**.

experimental ESR spectrum (Figure 4c) is a superposition of the spectra of many rotamers with slightly different E_Q values, resulting in a considerable line broadening of some signals and complete disappearance of other signals. Fortunately, the large E_Q strain effects do not affect the resonance field of several characteristic ESR signals of quintet dinitrenes. Thus, in the case of dinitrene **20**, two X transitions at 2995 and 8224 G and two off-principal-axis transitions at 2765 and 5880 G preserve their resonance fields almost unchanged, which allows one to determine the magnetic parameters of this dinitrene with high accuracy.

CONCLUSION

Photolysis of 2,6-bis(4'-azidophenyl)-4-phenylpyridine (**18**) in 2MTHF glass at 7 K produces quintet 2,6-bis(4'-nitrenophenyl)-4-phenylpyridine (**20**) as a mixture of rotational isomers. The ESR spectrum of this dinitrene shows a considerable broadening of many transitions and can only be simulated using the line-broadening parameter $\Gamma(E_Q) = 1200$ MHz (~ 430 G) along with the spin Hamiltonian parameters $g = 2.003$, $D_Q = 0.154$ cm $^{-1}$, and $E_Q = 0.050$ cm $^{-1}$. Other effects, such as g or D_Q strain effects, do not play a noticeable role in the ESR spectrum of **20**.

The most accurate theoretical estimations of the magnetic parameters of dinitrene **20** in a 2MTHF glass are obtained from PBE/DZ/COSMO//B3LYP/6-311+G(d,p) calculations of the parameters D_{SS} and E_{SS} . These calculations overestimate the E_Q and D_Q values of **20** by only 1% and 10%, respectively, demonstrating that contributions of D_{SOC} and E_{SOC} to the total D_Q and E_Q values of this dinitrene are negligibly small. Quite large (10%) divergence between the experimentally determined D_Q and theoretically predicted D_{SS} indicates specific interactions of dinitrene **20** with 2MTHF. The most stable rotamer of dinitrene **20** has the phenyl rings twisted from the plane of the pyridine ring by 19.8°; however, there are many other isomers of almost the same energy within a twisting angle of $\pm 30^\circ$. All these isomers have slightly different orientations of the principle magnetic axes D_X , D_Y , and D_Z of the triplet nitrene units and, as a result, slightly different parameters D_Q and E_Q .

Theoretically, polynuclear aromatic systems like **20** can have up to 11 high-spin coupled nitrene units, 9 of them on the side phenylnitrene rings and 2 others on the pyridine ring. The current study shows that ESR spectra of such multispin systems can be successfully analyzed only if large E_Q strain effects are taken into account in the spectral simulations.

ASSOCIATED CONTENT

S Supporting Information. B3LYP/6-311+G(d,p)-optimized structures and PBE/DZ-calculated orientations of the tensor D_Q of syn and anti isomers of quintet dinitrene **20**, all possible ESR spectral simulations reproducing the major signal of dinitrene **20** at 2995 G, and ESR spectra of dinitrene **20** predicted at the PBE/DZ level of theory from the ORCA program package. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) (a) Kalgutkar, R. S.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 4771–4772. (b) Miura, Y.; Oka, H.; Teki, Y. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 385–386. (c) Kalgutkar, R. S.; Lahti, P. M. *Tetrahedron Lett.* **2003**, *44*, 2625–2628.

- (2) (a) 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. (b) Chapyshev, S. V.; Walton, R.; Lahti, P. M. *Mendeleev Commun.* **2000**, *10*, 114–115. (c) Chapyshev, S. V.; Tomioka, H. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2075–2089. (d) Chapyshev, S. V.; Walton, R.; Serwinski, P. R.; Lahti, P. M. *J. Phys. Chem. A* **2004**, *108*, 6643–6649. (e) Chapyshev, S. V.; Lahti, P. M. *J. Phys. Org. Chem.* **2006**, *19*, 637–641. (f) Chapyshev, S. V. *Russ. Chem. Bull.* **2006**, *55*, 1126–1131. (g) Chapyshev, S. V. *Russ. Chem. Bull.* **2006**, *55*, 1593–1597.
- (3) Misochko, E. Ya.; Akimov, A. V.; Chapyshev, S. V. *J. Chem. Phys.* **2008**, *128*, 124504.
- (4) Chapyshev, S. V.; Walton, R.; Sanborn, J. A.; Lahti, P. M. *J. Am. Chem. Soc.* **2000**, *122*, 1580–1588.
- (5) (a) 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. (b) Misochko, M. Ya.; Akimov, A. V.; Chapyshev, S. V. *J. Chem. Phys.* **2008**, *129*, 174510. (c) Chapyshev, S. V.; Grote, D.; Finke, C.; Sander, W. *J. Org. Chem.* **2008**, *73*, 7045–7051. (d) Chapyshev, S. V.; Misochko, E. Ya.; Akimov, A. V.; Dorokhov, V. G.; Neuhaus, P.; Grote, D.; Sander, W. *J. Org. Chem.* **2009**, *74*, 7238–7244. (e) Chapyshev, S. V.; Neuhaus, P.; Grote, D.; Sander, W. *J. Phys. Org. Chem.* **2010**, *23*, 340–346.
- (6) Neese, F. ORCA, an *ab initio*, density functional and semiempirical program package, Version 2.8.0.1: University of Bonn: Bonn, Germany, 2010. The program was downloaded from <http://www.thch.uni-bonn.de/tc/orca>.
- (7) (a) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547–5556. (b) Sasaki, S.; Iwamura, H. *Chem. Lett.* **1992**, 1759–1762. (c) Ling, C.; Minato, M.; Lahti, P. M.; van Willegen, H. *J. Am. Chem. Soc.* **1992**, *114*, 9959–9969. (d) Minato, M.; Lahti, P. M.; van Willegen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532–4539. (e) Ling, C.; Lahti, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 8784–8792. (f) Ling, C.; Lahti, P. M. *Chem. Lett.* **1994**, 1357–1360.
- (8) Oda, N.; Nakai, T.; Sato, K.; Shiomi, D.; Kozaki, M.; Okada, K.; Takui, T. *Mol. Cryst. Liq. Cryst.* **2002**, *376*, 501–506.
- (9) (a) Koto, T.; Sato, K.; Shiomi, D.; Toyota, K.; Itoh, K.; Wasserman, E.; Takui, T. *J. Phys. Chem. A* **2009**, *113*, 9521–9526. (b) Koto, T.; Sugisaki, K.; Sato, K.; Shiomi, D.; Toyota, K.; Itoh, K.; Wassermann, E.; Lahti, P. M.; Takui, T. *Appl. Magn. Reson.* **2010**, *37*, 703–736.
- (10) Gavrishova, T. N.; Li, V. M.; Budyka, M. F. *Russ. J. Appl. Chem.* **2010**, *83*, 926–928.
- (11) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.
- (12) Fisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Stain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonczales, C.; Pople, J. A. *Gaussian 03*, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.
- (13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (14) (a) Pederson, M. R.; Khanna, S. N. *Phys. Rev. B* **1999**, *60*, 9566–9572. (b) Sinneker, S.; Neese, F. *J. Phys. Chem. A* **2006**, *110*, 12267–12275. (c) Neese, F. *J. Chem. Phys.* **2007**, *127*, 164112.
- (15) (a) Klamt, A.; Schuurman, G. *Perkin Trans.* **1993**, 799–805. (b) Sinneker, S.; Rajendran, A.; Klamt, A.; Diedenbafen, M.; Neese, F. *J. Phys. Chem. A* **2006**, *110*, 2235–2245.
- (16) Misochko, E. Ya.; Korchagin, D. V.; Bozhenko, K. V.; Chapyshev, S. V.; Aldoshin, S. M. *J. Chem. Phys.* **2010**, *133*, 064101.
- (17) The discontinuity at $\omega = 111^\circ$ is caused by a sudden structural reorganization of the molecule due to increasing steric hindrance between two phenylnitrene rings. This is not relevant for the results since only the distribution of the calculated values as a function of ω is discussed, not individual values.
- (18) Sugisaki, K.; Toyota, K.; Sato, K.; Shiomi, D.; Kitagawa, M.; Takui, T. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6970–6980.
- (19) Examples of simulated ESR spectra for quintet spin states with $g = 2.003$, $D_T = 0.91 \text{ cm}^{-1}$, and $E_Q/D_Q = 0.297$ and 0.305 are presented in the Supporting Information.