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Photochemical synthesis and ESR spectra of quintet *meta*-phenylenedinitrenes

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Relationships between the molecular structures and zero-field splitting parameters of quintet *m*-phenylenedinitrenes formed during the photolysis of 1,3-diazidobenzenes in 2-methyltetrahydrofuran solutions frozen at 77 K were studied by ESR spectroscopy and B3LYP/6-31G* calculations. Simulations of the W_{-2}/W_{-1}, W_{+2}/W_{+1}, W_{-1}/W_0, W_{+1}/W_0, and W_{+2}/W_0 ($\Delta m_s = 2$) transitions were performed for the first time and all signals in the ESR spectra of quintet *m*-phenylenedinitrenes were unambiguously assigned.

Key words: azides, nitrenes, photolysis, ESR spectroscopy, high-spin states.

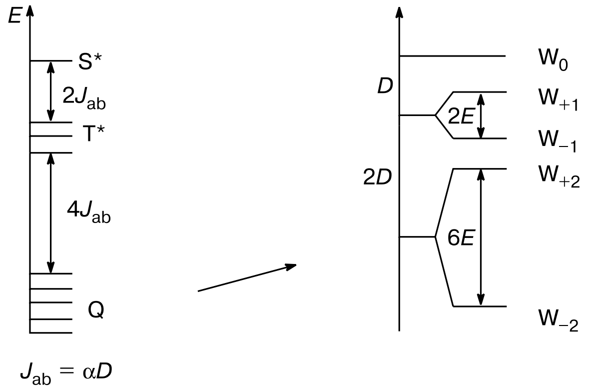

Fig. 1. Splitting of energy levels and sublevels in quintet ground spin state.

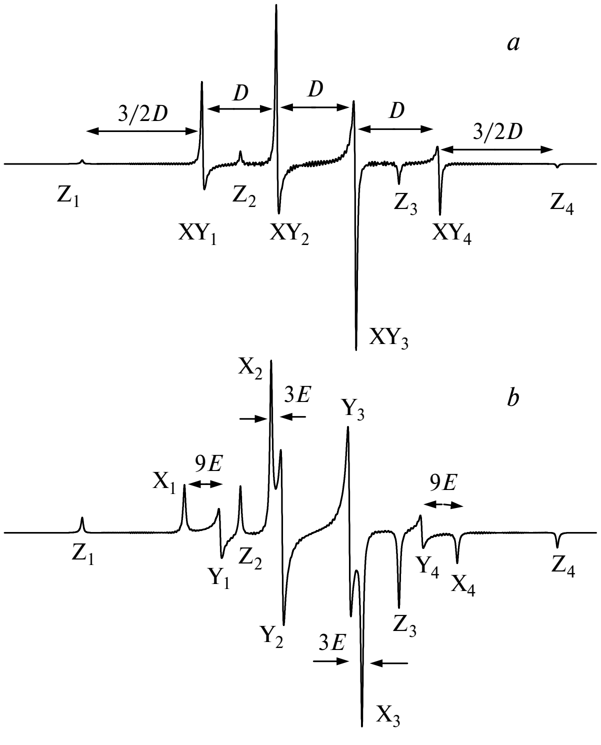

Fig. 2. Line splitting in ESR spectra of quintet molecules with $|E_q| = 0$ (*a*) and $|E_q| > 0$ (*b*).

Recently, considerable attention has been paid to quintet dinitrenes (QDNs) considered as promising organic magnetic materials for electronics.[1—4] These compounds are prepared by low-temperature solid-phase photolysis of aromatic diazides. Nitrenes isolated in the solid phase are stable at room temperature and form a magnetic sublattice with a large noncompensated magnetic moment.[5] The main method of spectroscopic identification of QDNs is ESR spectroscopy, which makes it possible to determine the zero-field splitting parameters D_q and E_q of five sublevels (W_{-2}, W_{+2}, W_{-1}, W_{+1}, and W_0) and to use them for structure elucidation and assessment of the stabilities, reactivities, and magnetic properties of these tetraradicals. Theory[6] predicts that the ground-state quintet and the excited-state triplet and singlet levels, quintet sublevels, and the lines corresponding to the X-, Y-, and Z-transitions in the ESR spectra of the quintet spin states are split as shown in Figs 1 and 2. The relatively simple first-order ESR spectra shown in Fig. 2 are observed only for the quintet molecules with $D_q < 0.01$ cm^{-1}.[6] The Z_4, X_1, and Y_1 lines correspond to transitions between the W_{-2} and W_{-1} levels and the lines Z_1, X_4, and Y_4 correspond to transitions between the W_{+1} and W_{+2} levels. More intense signals Z_3, X_2, and Y_2 characterize transitions between the W_{-1} and W_0 levels and the signals Z_2, X_3, and Y_3 correspond to transitions between the W_0

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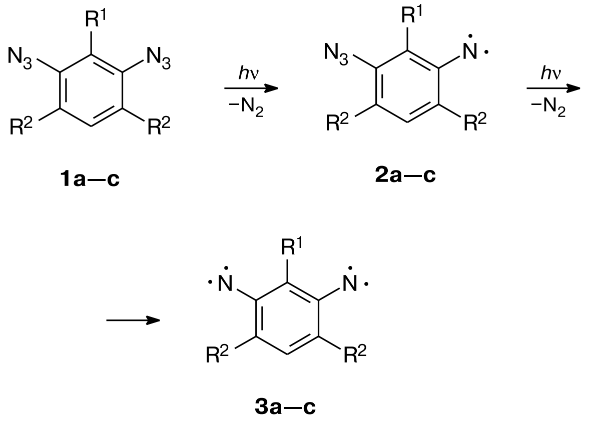
and W_{+1} levels. In the case of a quintet ground state, the signals in the left part of the ESR spectrum are more intense due to higher populations of the W_{-2} and W_{-1} levels.[6] Quintet dinitrenes are characterized by high spin density on the radical centers and by the largest D_q parameters among all the known quintet tetraradicals ($D_q > 0.15$ cm^{-1}). As a consequence, their ESR spectra are strongly different from the first-order spectra, being very difficult to analyze.[1]

For long, all calculations of the parameters D_q and E_q of quintet dinitrenes were carried out assuming that the QDN signals in the ESR spectra in a range of 8000—8800 G correspond to the Z_4-transition and the next signals of the X_4-transition match those of the X_2,Y_2-transition of intermediate triplet azidonitrenes in the range 6500—7500 G (see Refs 7 and 8). However, as modern programs for calculating ESR spectra have become available in the mid-1990s, it was established that all the D_q and E_q parameters of quintet dinitrenes reported earlier are incorrect.[9,10] Nevertheless, exact values of the parameters D_q and E_q for most QDNs known at the moment were not established so far. Moreover, no signal assignment in the ESR spectra of quintet dinitrenes, substantiated by calculating particular transitions W_{-2}/W_{-1}, W_{+2}/W_{+1}, W_{-1}/W_0, W_{+1}/W_0, and W_{-2}/W_0 ($\Delta m_s = 2$) was reported to date. The lack of this information considerably narrows down the potentialities of ESR spectroscopy for unambiguous identification of all paramagnetic products from photolysis of aromatic diazides.

In this study, relationships between the molecular structure and zero-field splitting parameters of quintet dinitrenes obtained from photolysis of corresponding diazides in 2-methyltetrahydrofuran (MTHF) solutions frozen at 77 K was studied by ESR spectroscopy and B3LYP/6-31G* calculations. Photochemical transformations of diazides **1a—c** resulting in nitrenes **2a—c** and dinitrenes **3a—c** are shown in Scheme 1.

Scheme 1



a: $R^1 = R^2 = H$; **b:** $R^1 = Me$, $R^2 = H$; **c:** $R^1 = R^2 = Me$

Experimental

Diazides **1a—c** were synthesized from the corresponding diamines following a known procedure.[11]

ESR spectra were recorded on a JEOL JES-TE200D instrument in the range 0—10000 G in MTHF solutions frozen at 77 K. The ESR spectra of paramagnetic products of photolysis of diazides **1a—c** were recorded at a microwave frequency of 9.243, 9.212, and 9.231 GHz, respectively. The experimental procedure involved the following steps. A weighed sample of a diazide (1 mg) was dissolved in 1 mL of MTHF freshly distilled over $LiAlH_4$ and placed in a 4-mm quartz ESR tube. The solution was degassed by carrying out three freeze (77 K)—pump ($5 \cdot 10^{-6}$ atm)—thaw cycles. The tube containing the degassed solution was filled with argon, sealed, and placed in a spectroscopic cell cooled to 77 K. A 1000-W high-pressure xenon lamp equipped with a 150-mm water filter served as a light source. The sample was placed at a distance of 30 cm from the light source and irradiated with light passed through a Pyrex filter. ESR spectra were recorded 0.5, 1, 2, 3, 4, 5, 10, 20, and 30 min after start of irradiation.

ESR spectra were calculated using a SIM ESR program for simulating the spectra of high-spin molecules randomly oriented in the solid phase.[12] Calculations were carried out assuming a *g*-factor of 2.0023 for all nitrenes. The zero-field splitting parameters of the triplet and quintet nitrenes were determined from theoretical (simulated) spectra, which exactly matched the experimental ESR spectra.

The geometric parameters of and the spin density distribution in the nitrene molecules were calculated by the UB3LYP/6-31G* method incorporated into the GAUSSIAN-94 program package.[13] All calculations were carried out with full optimization of the molecular geometries.

Results and Discussion

Photolysis of diazide **1a** (duration 4 min) led to the appearance of a characteristic signal of the X_2,Y_2-transition of triplet nitrene **2a** at 6830 G ($|D/hc| = 1.03$ cm^{-1} and $|E/hc| = 0$ cm^{-1}) and a set of signals of quintet dinitrene **3a** at 790, 1400, 3000, 3310, 3800, 4740, 6050, 6770, 8400, and 9820 G in the ESR spectrum (Fig. 3, *a*). The spectrum obtained almost exactly matched the ESR spectrum of paramagnetic products from photolysis of diazide **1a** reported earlier.[8] A new important observation made in this work is the detection of a weak signal of **3a** at 9820 G. It was accepted for long that the signal of radical **3a** at 8400 G is the outermost strong-field signal of this species corresponding to the line of the Z_4-transition and that the next signal of the X_4-transition is not observed due to the overlap with the signal of triplet nitrene **2a** at 6830 G (see Refs 7 and 8). Based on these assumptions,[7,8] it was concluded that quintet dinitrene **3a** is characterized by the parameters $|D/hc| = 0.156$—0.162 cm^{-1} and $|E/hc| = 0.025$—0.029 cm^{-1}. However, numerous attempts to simulate the ESR spectrum of dinitrene **3a** using these and other possible values of the parameters *D* and *E* failed. It was only reported that this quintet dinitrene

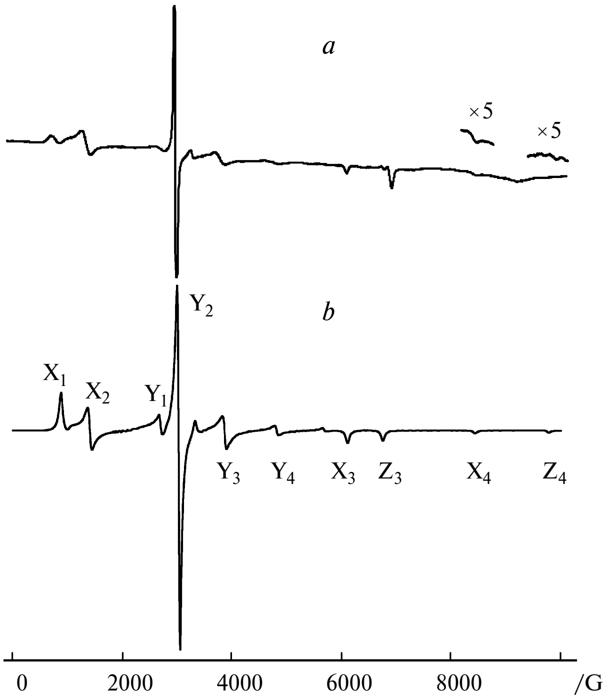


Fig. 3. ESR spectra of photolysis products of diazide **1a** (experiment, *a*) and a quintet spin state with the parameters $g = 2.0023$, $|D/hc| = 0.202$ cm^{-1}, and $|E/hc| = 0.040$ cm^{-1} (calculated using the SIM ESR program, *b*).

seems to have the parameter D of the order of 0.2 cm^{-1} and that its signal at 8400 G most probably corresponds to lines of the X_4-transition.[9] Detection of a very weak signal at 9820 G provides the first experimental substantiation of the fact that the lines of the X_4- and Z_4-transitions of dinitrene **3a** are observed at 8400 and 9820 G, respectively. According to calculations of the ESR spectra using the SIM ESR program, the parameters D_q and E_q of dinitrene **3a** are 0.202 and 0.040 cm^{-1}, respectively (Fig. 3, *b*). The first-time-simulated ESR spectrum of quintet dinitrene **3a** quite correctly reproduces the experimental spectrum (see Fig. 3, *a*). Similar ESR spectra are characteristic of most QDNs with *meta*-orientation of nitrene centers in the aromatic ring.[1] Exact D_q and E_q values obtained from simulation for radical **3a** indicate that this pattern of the ESR spectra is characteristic of quintet molecules with the $|E_q/D_q|$ ratio of the order of 0.2.

Photolysis of diazide **1b** over a period of 20 min led to the appearance of a characteristic signal of the X_2,Y_2-transition of triplet nitrene **2b** at 6740 G ($|D/hc| =$ 0.99 cm^{-1} and $|E/hc| = 0$ cm^{-1}) and signals of radical **3b** at 890, 1650, 2370, 2930, 3990, 5050, 5930, 8130, and 9650 G in the ESR spectrum (Fig. 4, *a*). Simulation of ESR spectra showed that the parameters D_q and E_q of radical **3b** are equal to 0.198 and 0.034 cm^{-1}, respectively (Fig. 4, *b*). A similar ESR spectrum was also observed in the photolysis of diazide **1c** over a period of 10 min (Fig. 5, *a*). The characteristic signal of the X_2,Y_2-transition of triplet nitrene **2c** appeared at 6580 G ($|D/hc| = 0.93$ cm^{-1} and $|E/hc| = 0$ cm^{-1}) and the signals of radical **3c** were observed at 720, 1660, 2650, 2890, 3790, 4760, 5780, 6340,

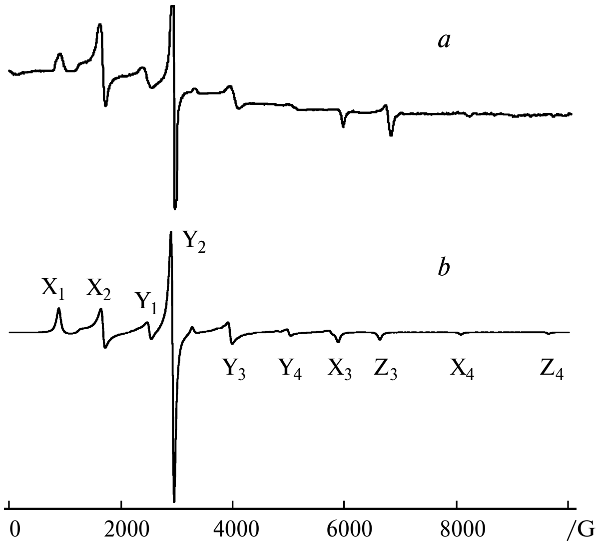


Fig. 4. ESR spectra of photolysis products of diazide **1b** (experiment, *a*) and a quintet spin state with the parameters $g = 2.0023$, $|D/hc| = 0.198$ cm^{-1}, and $|E/hc| = 0.034$ cm^{-1} (calculated using the SIM ESR program, *b*).

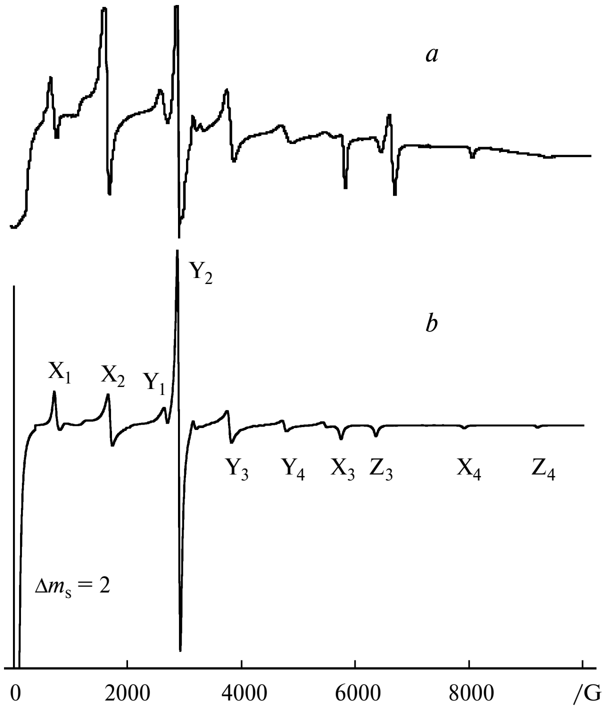


Fig. 5. ESR spectra of photolysis products of diazide **1c** (experiment, *a*) and a quintet spin state with the parameters $g = 2.0023$, $|D/hc| = 0.184$ cm^{-1}, and $|E/hc| = 0.035$ cm^{-1} (calculated using the SIM ESR program, *b*).

7930, and 9200 G. The calculated parameters D_q and E_q of quintet dinitrene **3c** are 0.184 and 0.035 cm^{-1}, respectively (Fig. 5, *b*).

The observed ESR spectra of dinitrenes **3a—c** are typical of the QDNs with *meta*-orientation of the nitrene centers in the aromatic ring and the vector angles θ between two C—N bonds varying between 118 and 125°.[7—10] High intensities of the signals in the left part of the spectra proves that radicals **3a—c** are in the quintet ground states. Due to very large parameters D_q the spectra of these compounds are strongly different from the first-order ESR spectra. Besides, large parameters E_q of these compounds also affect the spectral pattern, namely, they radically change the intensities and mutual positon of many signals.

Until recently, it was accepted[9] that many signals in the ESR spectra of the QDNs with $118 < \theta < 125°$ belong to molecules with non-canonical orientation of the magnetic axes. This first of all concerned the most intense signals at 2900—3000 G, intense signals at 3600—3800 G, and signals in the range 5700—6100 G. Additionally, it was possible that certain signals belong to other paramagnetic products of photolysis of diazides.[9] In order to establish how many and what paramagnetic products are formed in the photolysis of diazides **1a—c**, we calculated the ESR spectra for particular transitions, namely, W_{-2}/W_{-1}, W_{+2}/W_{+1}, W_{-1}/W_0, W_{+1}/W_0, and W_{+2}/W_0 taking dinitrene **3c** as an example (Fig. 6). According to calculations, the most intense signal at 2890 G corresponds to the line of the Y_2-transition, the next in intensity signal at 1660 G corresponds to the line of the X_2-transition, and the signal of medium intensity at 6340 G corresponds to the line of the Z_3-transition. It is these three signals that are most pronounced in the ESR spectra of most QDNs with *meta*-orientation of the nitrene centers in the aromatic ring.[1,7—10] As expected, the weak signal at 9200 G corresponds to the line of the Z_4-transition, and the next signal at 7820 G corresponds to the line of the X_4-transition. These signals are of great importance because they allow the parameters D_q and E_q for quintet dinitrenes to be calculated with high accuracy from known equations.[7] Full signal assignment in the ESR spectrum of dinitrene **3c** is shown in Fig. 5, *b*. A very intense signal, which appears as a broad band with negative intensity in the weakest field, deserves particular attention. According to calculations, this band corresponds to the line of the transition with $\Delta m_s = 2$ (see Fig. 6, *a*). As far as we know, this is the first example of detection of a line of the transition with $\Delta m_s = 2$ for QDNs. By and large the absence of any signals except those of triplet azidonitrene **2c** and quintet dinitrene **3c** in the ESR spectrum obtained after photolysis of diazide **1c** provides a rigorous proof that only these two compounds are paramagnetic products of the reaction. This also holds for the photolysis of diazides **1a** and **1b** (see Figs 3 and 4, respectively).

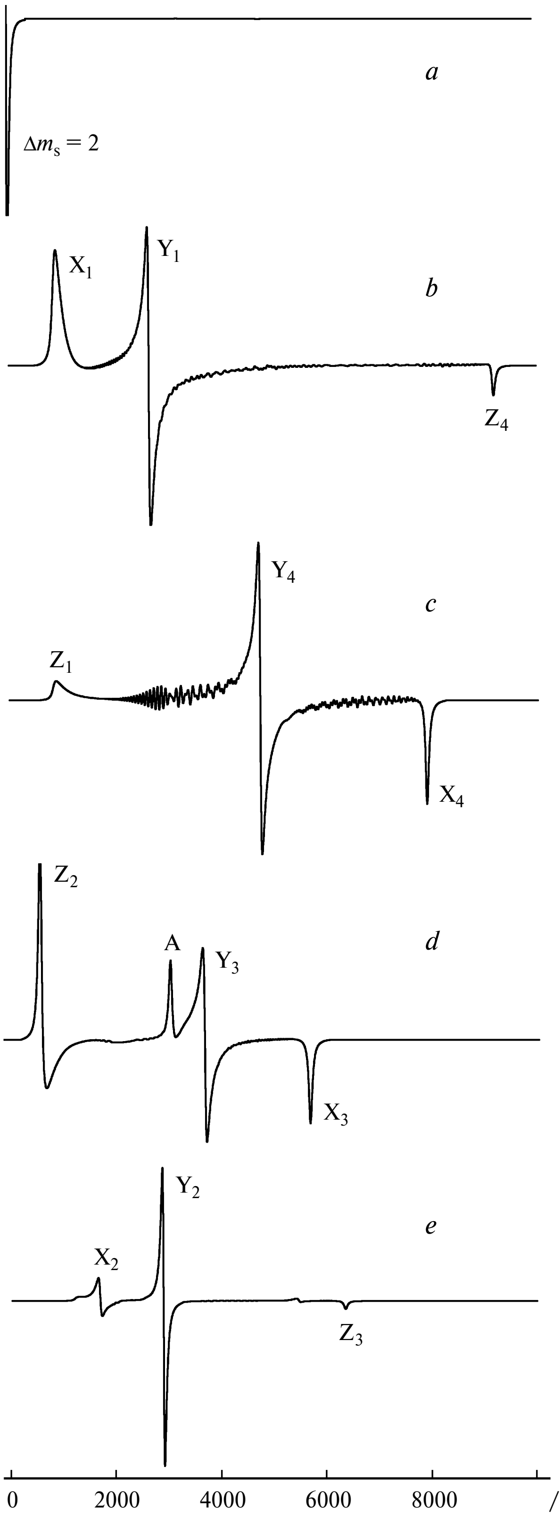


Fig. 6. Lines corresponding to transitions W_{-2}/W_0 (*a*), W_{-2}/W_{-1} (*b*), W_{+1}/W_{+2} (*c*), W_{+1}/W_0 (*d*), and W_0/W_{-1} (*e*) in the ESR spectrum of quintet dinitrene **3c** (A is the transtion line for a molecule with non-canonical orientation of magnetic axes).

In order to study relationships between the structure and spectral characteristics of the nitrenes in question, we

Table 1. Zero-field splitting parameters (D_T, E_T, D_q, E, and D_t), spin densities on nitrene centers (ρ_N), and vector angles (θ) compounds **2a—c** and **3a—c**

Nitrene	D_T	E_T	D_q	E_q	D_t	θ/deg	ρ_N
	cm^{-1}						
2a	1.030	0.000	—	—	—	—	1.6125
2b	0.990	0.000	—	—	—	—	1.5953
2c	0.930	0.000	—	—	—	—	1.5423
3a	—	—	0.202	0.040	0.957	120.7	1.5980
3b	—	—	0.198	0.034	0.892	123.6	1.5790 1.5661
3c	—	—	0.184	0.035	0.862	121.0	1.5651 1.5333

carried out B3LYP/6-31G* quantum chemical calculations of geometric parameters and spin density distribution for triplet nitrenes **2a—c** and quintet dinitrenes **3a—c** (Table 1). According to calculations, an increase in the number of methyl groups in the aromatic ring causes a decrease in the spin density on the nitrene centers of the triplet and quintet nitrenes. This is in good agreement with the decrease in the parameters D of triplet nitrenes **2a—c** and quintet dinitrenes **3a—c**. Besides, the lower the spin density on the radical center the lower the reactivity of the radical.[14] Clearly, high intensity of the ESR spectra of nitrene **2c** and dinitrene **3c** is due to relatively low reactivities of these compounds, which are the least prone to undergo side transformations resulting in diamagnetic products under the photolysis conditions. Dinitrenes **3a—c** with different angles θ and spin densities on the nitrene centers are interesting objects for studying the effect of these two factors on the spectral characteristics of QDNs. Earlier,[15] it was shown that the D_q and E_q parameters of quintet dinitrenes can be quite correctly calculated using Eqs (1) and (2)

$$D_q = D_t(3\sin^2\alpha - 1)/6, \quad (1)$$

$$E_q = D_t(\cos^2\alpha)/6, \quad (2)$$

where α is θ/2, and D_t is the parameter D of the biradical nitrene center in the quintet molecule.

However, calculations of the parameters D_q and E_q for quintet dinitrenes from Eqs (1) and (2) were strongly complicated by the lack of any experimental and theoretical methods for exact determination of the values of the parameters D_t. Therefore, it was accepted[15] that the parameters D_t of quintet dinitrenes are nearly equal to the parameters D_T of intermediate triplet azidonitrenes formed in the photolysis of diazides. Indeed, our calculations confirm that the spin densities on the nitrene centers in the pairs **2a**/**3a**, **2b**/**3b**, and **2c**/**3c** differ insignificantly. However, a comparison between the properties of triplet nitrenes **2a** and **2b** shows that an increase in the spin density on the nitrene center even by 0.01 causes an increase in the parameter D_T by 0.04 cm^{-1}. The exactly determined parameters D_q and E_q and the calculated values of the angles θ for dinitrenes **3a—c** for the first time make it possible to calculate the parameters D_t from Eqs (1) and (2). For dinitrenes **3a**, **3b**, and **3c** they are equal to 0.957, 0.892, and 0.862 cm^{-1}, respectively, which is much lower than the parameters D_T of triplet azidonitrenes **2a**, **2b**, and **2c** (see Table 1). It should be noted that the D_t values obtained for dinitrenes **3b** and **3c** having different spin densities on the nitrene centers are the mathematically averaged values D_t^1 and D_t^2 for the inequivalent nitrene centers. We estimated the D_t values of the nitrene centers with spin densities of 1.6, 1.58, 1.57, and 1.53 in QDNs at 0.95—0.96, 0.89—0.90, 0.87—0.88, and 0.83—0.84 cm^{-1}. These ratios can be useful for spectral identification of quintet products of photolysis of aromatic diazides by ESR spectrocopy, especially in those cases where photolysis results in a complex mixture of dinitrene isomers.

In this work we established that QDNs with the spin densities on the nitrene centers from 1.53 to 1.60 and the vector angles between two nitrene C—N bonds from 120 to 124° are characterized by the parameters D_q in the range 0.184—0.202 cm^{-1} and E in the range 0.034—0.040 cm^{-1}. Full assignment of all signals in the ESR spectra of quintet dinitrenes unambiguously proves that paramagnetic products of photolysis of 1,3-diazidobenzenes includes only corresponding triplet azidonitrenes and quintet dinitrenes.

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