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Intermediates of photolysis of 1,3,2,4-benzodithiadiazines studied by matrix isolation spectroscopy and quantum chemistry

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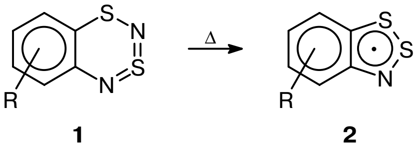
Photolysis of 12π-electron, formally antiaromatic, 1,3,2,4-benzodithiadiazine (**1a**) and its tetrafluoro-substituted derivative (**1b**) was studied in glassy matrices at 77 K and in an argon matrix at 14 K by UV, IR, and ESR spectroscopy. In these matrices, a diamagnetic species (**3a,b**) is formed as a persistent species. It is product of the intramolecular transformations of heterocycles **1a,b** and the precursor of 1,2,3-benzodithiazolyl radicals (**2a,b**). The nitrenoid structure, intermediate between the structures of singlet 1,2,3-benzodithiazol-2-ylnitrene RS—N: and the corresponding thiazyl RS≡N, was ascribed to intermediate **3a,b** in agreement with the data of IR spectroscopy.

Key words: 1,3,2,4-benzodithiadiazine, 1,2,3-benzodithiazolyl radical, 1,2,3-benzodithiazol-2-ylnitrene, photolysis, UV spectroscopy, IR spectroscopy, ESR spectroscopy, matrix isolation, quantum yield, *ab initio* quantum-chemical calculations.

1,3,2,4-Benzodithiadiazine (**1a**) and its substituted derivatives constitute a new and poorly studied class of compounds.[1—3] These substances are formally antiaromatic[4] because in the nearly planar molecular geometry (in both the gas phase[5] and crystalline state[1—3,6]) they possess the cyclic 12π-electron system,[7] low-lying excited states,[1—3,6] and an enhanced magnetic shielding[1,3,6] of the nuclei closest to the heterocycle H(5) and H(8) possibly due to paratropic circular currents.[4] Very little information about the chemical properties of 1,3,2,4-benzodithiadiazines has been published recently. It is known that they react with triphenylphosphine and dichloromonosulfane to form the oxidative imination products of phosphorus and sulfur, respectively,[6,8] which demonstrate nitrenoid reactivity.

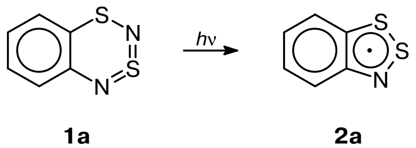
It has recently[9,10] been found that during thermolysis, under mild conditions (110—150 °C), **1a** and many its derivatives, including the tetrafluoro derivative (**1b**), are transformed into stable 1,2,3-benzodithiazolyl radicals (**2**) in almost 100% yield (Scheme 1). The latter are of special interest because can be used in the synthesis of organic molecules with the high-spin ground state (molecular magnetics).[11,12]

Scheme 1



Photolysis[10] of **1a** in hydrocarbon solvents at room temperature also results in the formation of the 1,2,3-benzodithiazolyl radical (**2a**) in a yield close to 100% (Scheme 2).

Scheme 2



The transformation of 1,3,2,4-benzodithiadiazines (**1**) into 1,2,3-benzodithiazolyl radicals **2** is a nontrivial process requiring the contraction of the ring and loss of the nitrogen atom. It occurs, evidently, in several stages. It is of interest that the photolysis (300 nm) of the closest 10- and 14π-electron analogs, 1,2,3-benzo-

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thiadiazole[13] and 1,3,5,2,4-benzotrithiadiazepine,[14] is accompanied by the elimination of the sulfur atom (and also carbocycle opening for thiadiazole), resulting in the formation of hexa-2,4-dienedinitrile[13] and unidentified products,[14] respectively.

This work is devoted to revealing the nature of intermediate species appeared by the photolysis of 1,3,2,4-benzodithiadiazine. The methods of matrix isolation, low-temperature photolysis, and quantum chemistry were used for the solution to the problem.

Experimental

Reagents and solvents. 1,3,2,4-Benzodithiadiazine (**1a**) and its 5,6,7,8-tetrafluoro derivative (**1b**) were synthesized according to described procedures.[1,2] 2,6,10,15,19,25-Hexamethyltetracosane (squalane, Aldrich), methylcyclohexane (Aldrich), hexane (reagent grade), and benzene (reagent grade) were used as solvents.

Photolysis at room temperature. Solutions (*ca.* 10^{-3} mol L^{-1}) of **1a** or **1b** in squalane, benzene, or hexane were placed into a quartz cylindrical ampule 4 mm in diameter (for detection of ESR spectra) and degassed by repeating a freeze—pump—thaw procedure three times. In the case of recording electronic absorption spectra (EAS), 1-cm quartz cells were used, and oxygen was removed by bubbling argon through the solution for 20 min. Irradiation was conducted by the filtered light from a high-pressure DRSh-500 mercury lamp. Individual lines of a mercury lamp (313, 365, and 436 nm) were separated by a combination of glass filters. Photolysis quantum yields were measured using the isomerization of 2-dialkylamino-1,4-naphthoquinones[15] as an actinometric photoreaction with a quantum yield of 0.1 for the photoisomerization of 2-dimethylamino-3-chloro-1,4-naphthoquinone in benzene.[16]

ESR spectra were recorded on a Bruker EMX spectrometer. EAS were recorded on a Specord UV-Vis spectrophotometer.

Spectroscopy in glassy solvents. Solutions ($(1-5)\cdot10^{-3}$ mol L^{-1}) of **1a** (or **1b**) in squalane or methylcyclohexane were placed in a thin-walled quartz cell 2 mm thick (EAS) or into a quartz cylindrical cell 4 mm in diameter (ESR spectra).

Photolysis and recording of EAS were carried out placing a cell into a quartz cryostat with planar-parallel windows filled with liquid nitrogen. Photolysis and ESR spectra recording were performed using a cylindrical quartz cryostat.

Spectroscopy in argon matrices. A gas mixture of **1a** or **1b** and argon was sputtered on the surface of CsI plate (layer thickness *ca.* 10^2 μm) cooled with helium from the closed cycle cryogenic system (Air Products). In order to prepare a gas mixture, an argon flow was passed above solid compounds **1a** or **1b** cooled to a certain temperature. This temperature in different experiments was varied within 255—295 K. The dilution of compounds **1a**, **1b** with the matrix substance was varied in the interval from 1 : 4000 to 1 : 500. In most experiments, this ratio was approximately 1 : 1000. The temperature of the argon matrix was maintained at 14 K. EAS were detected on a Lambda 6 UV-VIS spectrophotometer with the 1-nm resolution. IR spectra were recorded on a Perkin-Elmer FIT-IR 2000 Fourier spectrometer with a resolution of 0.2 cm^{-1}. Irradiation was performed with the light with a wavelength of 254 or 300 nm (Ray-o-Net lamps). EAS and IR spectra of samples were recorded before and during irradiation.

***Ab initio* quantum-chemical calculations.** The geometry of reactants, products, and assumed intermediates was optimized by the B3LYP method[17] using the 6-31G* basis set.[18] Harmonic frequencies calculated by the B3LYP/6-31G* method were used in analysis of experimental IR spectra. The solvent influence on the singlet-triplet splitting in 1,2,3-benzodithiazol-2-ylnitrene (**3a**) was applied using the polarized continuum model (PCM, Tomasi).[19] All calculations were performed using the GAUSSIAN 98 program package.[20]

Results and Discussion

*Photolysis of 1,3,2,4-benzodithiadiazine (**1a**).* The EAS of compound **1a** has a weak long-wavelength absorption band with a maximum at 618 nm ($\varepsilon = 400$ mol^{-1} L cm^{-1}) and several more intense bands in the UV spectral region (Fig. 1). The quantum yield of **1a** photodecomposition in benzene upon excitation at 436 nm does not exceed $3\cdot10^{-4}$ and increases considerably with an increase in the photon energy (Fig. 1).

It has previously been shown[10] that UV irradiation (365 or 313 nm) of hydrocarbon solutions of **1a** at room temperature affords the 1,2,3-benzodithiazolyl radical **2a** in almost quantitative (~95%) yield (Scheme 2). Radical **2a** and several its derivatives were also obtained in ~100% yields by the thermolysis of 1,3,2,4-benzodithiadiazines (Scheme 1).[9,10]

Photolysis (Fig. 2, *a*) and thermolysis (Fig. 2, *b*) of **1a** result in substantial changes in the EAS. The absorption in the long-wavelength spectral region decreases, and an intense band appears at 300—400 nm, which agrees with the published EAS of radical **2a**.[21] The shift of the isobestic point upon the prolonged irradiation of **1a** is associated, most likely, with the slow photodecomposition of radical **2a**.[10]

The spectral changes during the irradiation of a glassy solution of **1a** at 77 K (Fig. 3) differ substantially from those observed at room temperature (Fig. 2, *a*). At 77 K a species with an intense absorption band with

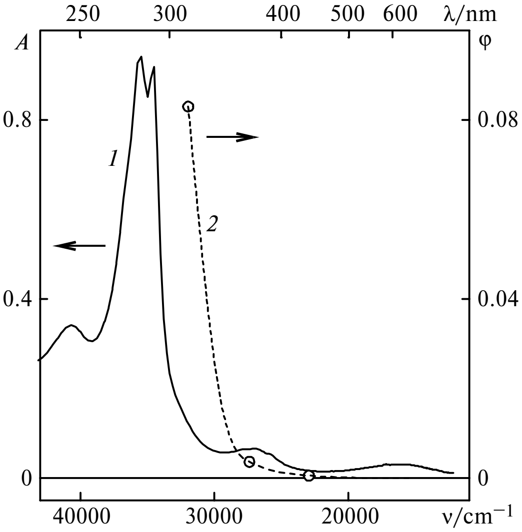


Fig. 1. Electronic absorption spectrum of compound **1a** in hexane (*1*, $C = 7.6\cdot10^{-3}$ mol L^{-1}) and the plot of the quantum yield (φ) of photolysis of **1a** in benzene at *ca.* 20 °C *vs.* excitation wavelength (*2*).

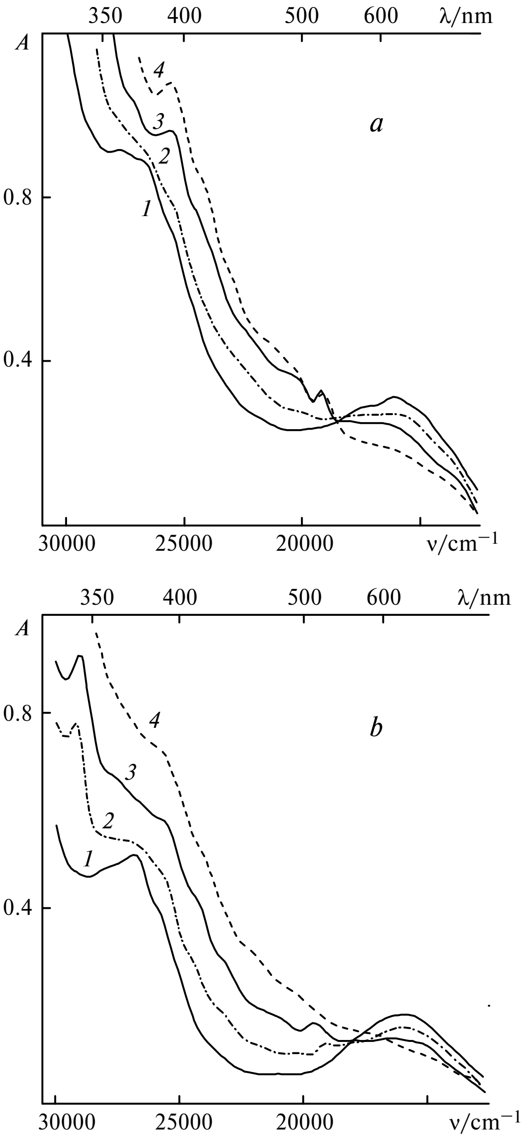


Fig. 2. (*a*) EAS of compound **1a** in squalane (*1*) and its change under irradiation with a wavelength of 313 nm at *ca.* 20 °C for 8 (*2*), 16 (*3*), and 30 min (*4*); (*b*) EAS of **1a** in squalane (*1*) and its change on heating to 140 °C for 30 (*2*), 70 (*3*), and 125 min (*4*). Spectra were registered at *ca.* 20 °C.

maxima at 445, 464, and 493 nm is formed and stabilized. It is most likely that these maxima are related to the vibrational structure of the spectrum. Heating of the sample to room temperature results in the disappearance of this band and the appearance of the spectrum characteristic of radical **2a**, which also is confirmed by the ESR data. Therefore, the species that formed is a precursor of radical **2a**. Since no signal in the 3000—8000 G region was observed in the ESR spectrum of the sample before thawing, this indicates its diamagnetic nature.

The same species was obtained by the photolysis of **1a** in the argon matrix. During the irradiation of **1a** in the argon matrix at 14 K, an intermediate species is

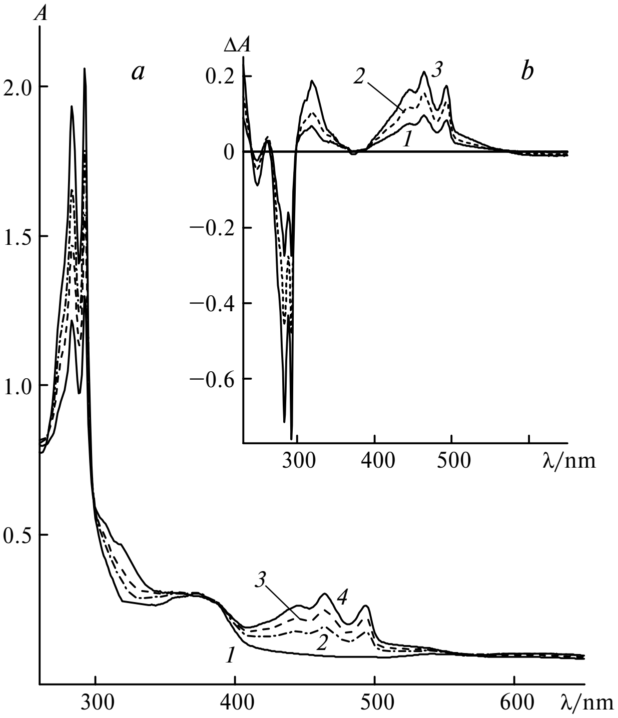


Fig. 3. (*a*) EAS of **1a** in methylcyclohexane (*1*) and its change upon photolysis at 77 K with a wavelength of 313 nm for 5 (*2*), 15 (*3*), and 40 min (*4*); (*b*) transient EAS of **1a** after irradiation for 5 (*1*), 15 (*2*), and 40 min (*3*).

formed and stabilized, whose EAS spectrum is presented in Fig. 4. Note that for small spectral changes (Fig. 4, curve *2*) the vibrational structure of the spectrum is not pronounced. In our opinion, this is related to experimental distortions due to the detection of a weak signal against the background of a considerable absorption and scattering of the support and matrix. For the detection

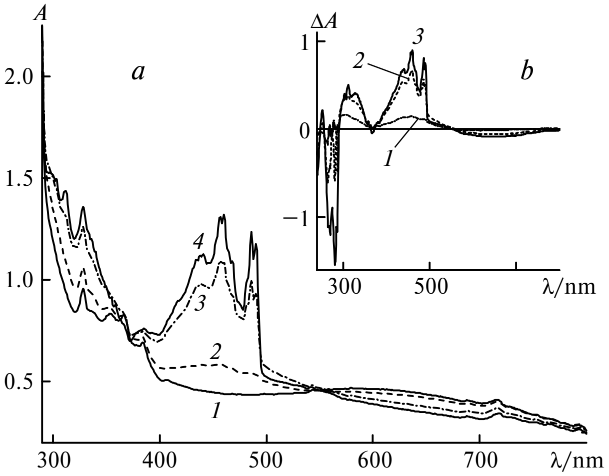


Fig. 4. (*a*) EAS of **1a** in the argon matrix at 14 K (*1*) and its change upon irradiation (300 nm) for 5 (*2*), 60 (*3*), and 150 min (*4*) (during the preparation of the sample, an Ar flow was passed above solid **1a** at 0 °C); (*b*) transient spectrum after irradiation for 5 (*1*), 60 (*2*), and 150 min (*3*).

of more considerable changes (curves *3* and *4*), the structure of the band detected at 77 K is well seen. The spectra recorded during photolysis in the methylcyclohexane matrix at 77 K (Fig. 3, curves *2—4*) and at 14 K in the argon matrix (curves *3* and *4*) virtually coincide. Therefore, the hydrocarbon matrix does not participate in the formation of a precursor.

IR spectra were obtained simultaneously with the detection of EAS in the argon matrix. Figure 5 presents the IR spectrum of the sample before irradiation (*1*) and its change observed 5 min after the beginning of irradiation (*2*). The IR spectrum of **1a** recorded at 14 K in the argon matrix is close to that detected previously[1,5] in pellets with KBr. The shift of most absorption bands does not exceed 3—4 cm^{-1}. Note that the IR spectrum of **1a** calculated by the B3LYP/6-31G* method (Fig. 5, curve *3*) very well agrees with the experimental one (Fig. 5, curve *1*) by both the position of bands and their relative intensity.

During photolysis intensities of all absorption bands of the initial compound **1a** decrease and several new absorption bands appear (Fig. 5, curve *2*). Note that not all newly appeared IR bands behave similarly. The bands marked by an asterisk appear in the first minutes of irradiation, their intensity increases in parallel with a decrease in the intensity of the absorption bands of **1a** and remains unchanged during prolonged (*ca.* 1 h) irradiation with the long-wavelength light (650 nm). Unlike this, three rather intense lines in the transient spectrum at 1234, 1498, 1528 cm^{-1} (Fig. 5) are virtually absent at short irradiation times, and for prolonged irradiation their intensities increase rapidly. In addition, they completely disappear after 1-h irradiation with the light with 650 nm. Thus, only lines marked with asterisk

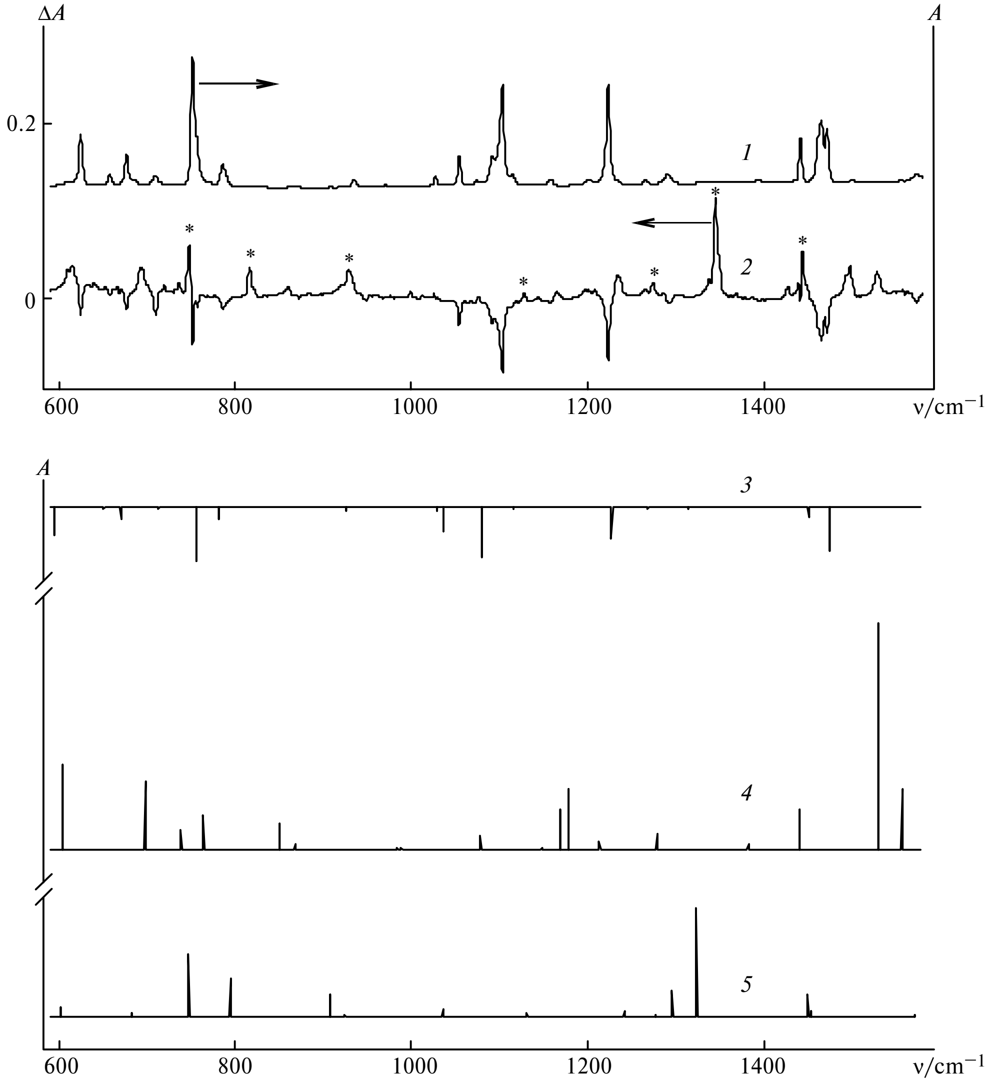
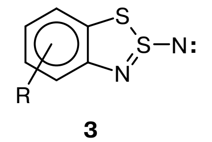


Fig. 5. IR spectrum of **1a** in the argon matrix at 14 K (*1*) and transient IR spectrum (*2*) after irradiation with 300 nm for 5 min (during the preparation of the sample, an Ar flow was passed above solid **1a** at *ca.* 20 °C); IR spectra calculated by the B3LYP/6-31G* method for compound **1a** (*3*), iminothiazyl **5a** (*4*), and 1,2,3-benzodithiazol-2-ylnitrene (**3a**) (*5*). All calculated frequencies were multiplied by a calibration factor of 0.98.

in the IR spectrum belong to the intermediate of phototransformations **1a** → **2a**, and other lines belong to products of its secondary photolysis. Note that in this work we do not intend to elucidate the nature of the secondary photolysis products.

Thus, the irradiation of **1a** in both the glassy matrix at 77 K and the argon matrix at 14 K results in the formation and stabilization of a diamagnetic species, which is a precursor of radical **2a**, *viz.*, the photolysis product at room temperature.

We have previously assumed[10] that the transformation of 1,3,2,4-benzodithiadiazines **1** into the final radical products **2** (Schemes 1 and 2) can proceed through intermediate singlet 1,2,3-benzodithiazol-2-ylnitrenes (**3**).



3

Singlet nitrene **3a** is the isomer of dithiadiazine **1a** and contains the same heterocyclic fragment as the resulting radical **2a**.

Comparison of the experimental IR spectrum of the photolysis product at 14 K (Fig. 5, curve *2*) with the calculated spectrum of nitrene **3a** (curve *5*) demonstrates their good agreement in both the position and the relative intensity of the bands.

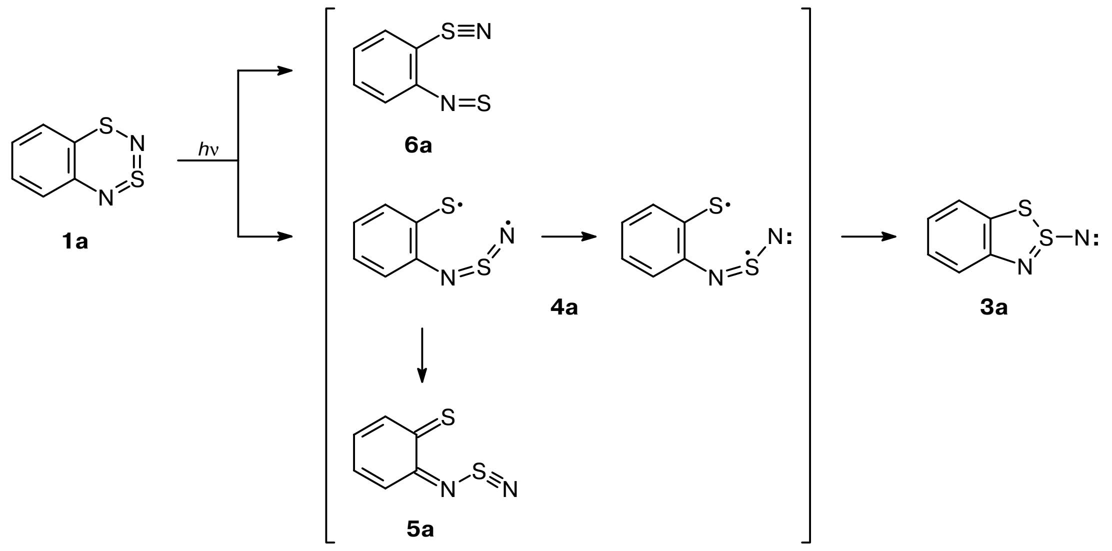
The formation of nitrene **3a** during the photolysis of **1a** also can occur in several stages. The observed dependence of the quantum yield on the irradiation wavelength (see Fig. 1) indicates that the photochemical transformations occur in the highly excited electronic state. Our previous[10] calculations of the EAS of compound **1a** showed that three long-wavelength transitions can be attributed to the ππ*-type, and the fourth transition (at 314 nm) is the transition of the πσ*-type, and molecule **1a** being excited in this state can readily dissociate.

It can be assumed that the primary process during the photolysis of **1a** is the cleavage of the S(1)—N(2) σ-bond (least stable in **1a**) and the formation of the S,N-biradical **4a** (Scheme 3). Note that due to the close electronegativities of the S and N atoms, the SN bonds are lowly polar and their homolytic cleavage is well known.[22] S,N-Biradical **4a** can further be reorganized into the S,S-biradical (Scheme 3) with the localization of an electron pair on the N(2) atom. Then the radical centers of the S,S-biradical recombine to form singlet 1,2,3-benzodithiazol-2-ylnitrene (**3a**).

Since the long-wavelength band in the EAS of the detected intermediate lies in the same region as that of very unstable and poorly studied thionitrosoarenes ArN=S (470—485 nm)[23,24] (in particular, 2-thionitrosonitrosobenzene isolated in the argon matrix during the photolysis of 1,2,3-benzothiadiazole *N*-oxide),[23] the participation of 2-thiazylthionitrosobenzene (**6a**) and quinoid iminothiazyl **5a** in the process considered can be assumed (Scheme 3), although the structures of these substances are far from that of radical **2a**. The calculated IR spectrum of iminothiazyl **5a** (Fig. 5, curve *4*) does not agree with that of the photolysis product in the argon matrix. The IR spectrum calculated for structure **6a** does not agree with experiment either.

*Photolysis of 5,6,7,8-tetrafluoro-1,3,2,4-benzodithiadiazine (**1b**).* When **1b** is irradiated at 77 K in the methylcyclohexane matrix and at 14 K in the argon matrix, a species is formed as a persistent species, whose electronic absorption spectrum is close to that appeared during the photolysis of **1a** (Figs. 3 and 4). The only distinction is that the vibrational structure is poorly pronounced and maxima are shifted to the red region by 6—8 nm. However, the IR spectra of compound **1b** and of its photolysis product in the argon matrix (Fig. 6), as should be expected, differ substantially from those presented in Fig. 5. The experimental spectrum of **1b** (Fig. 6, curve *1*) is close to the spectrum in KBr known from literature[2,5] and is well reproduced by the

Scheme 3



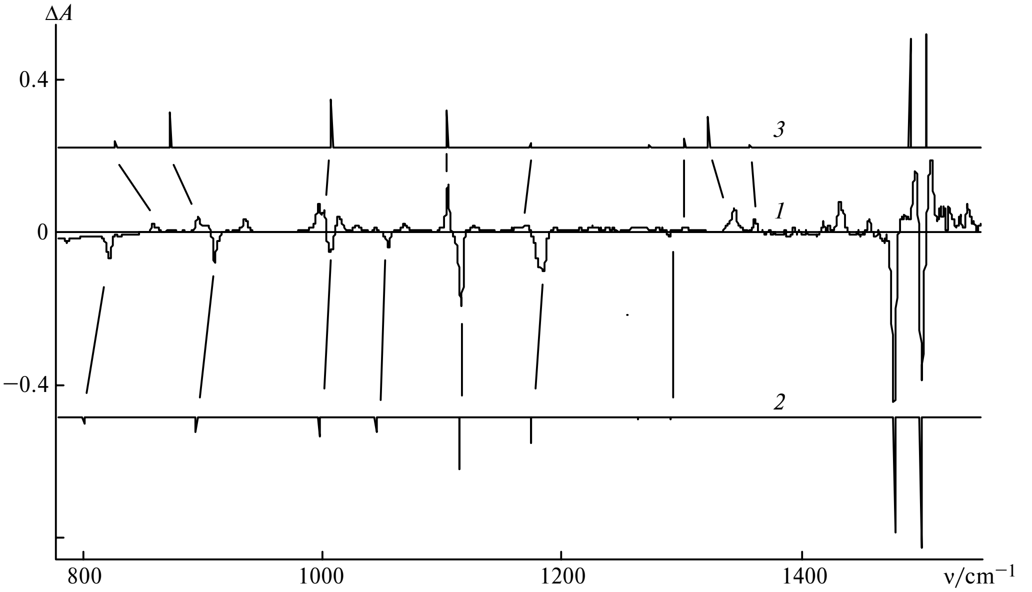


Fig. 6. Transient IR spectrum in the Ar matrix at 14 K (*1*) after the irradiation of compound **1b** for 5 min (λ = 300 nm). IR spectra calculated by the PB3LYP/6-31G* method for compound **1b** (*2*) and 5,6,7,8-tetrafluoro-1,2,3-benzodithiazol-2-ylnitrene (**3b**) (*3*). All calculated frequencies were multiplied by a calibration factor of 0.978.

B3LYP/6-31G* calculation (Fig. 6, curve *2*). In turn, the calculated spectrum of 5,6,7,8-tetrafluoro-1,2,3-benzodithiazol-2-ylnitrene (**3b**) agrees quite satisfactorily with the spectrum recorded after irradiation in the argon matrix. All of the most intense lines in the experimental spectrum (except the line at 1433 cm^{-1}) correspond to those in the calculated spectrum by the position and relative intensity.

*Quantum-chemical calculations of the structure and properties of 1,2,3-benzodithiazol-2-ylnitrene (**3a**).* It follows from experimental data that nitrenes **3a,b** in the ground singlet state are the species which are stabilized during the photolysis of **1a,b** in low-temperature matrices. It is known[25,26] that alkyl- and arylnitrenes have the ground triplet state. Unlike alkyl- and arylnitrenes, carbenes[27] can have either a triplet or a singlet ground state. Nitrenes in which the nitrogen atom is bound to an atom different from carbon are poorly studied.[25] Direct data on the detection of sulfenylnitrenes and theoretical calculations are lacking, although it has been assumed that the oxidation of benzenesulfenamides[28,29] affords substituted sulfenylnitrenes in the ground singlet state.

Our calculations showed that the singlet is, in fact, the ground state for nitrene **3a**. According to the B3LYP/6-31G* data, the triplet state is higher than the singlet state by 1.8 kcal mol^{-1} in the gas phase and by 4.5 kcal mol^{-1} in hexane. The calculated geometry of nitrene **3a** in the singlet state is presented in Fig. 7. For comparison, this figure also presents the geometry of radical **2a**. It has recently been shown[5] that the B3LYP method very well reproduces the structure of molecules **1a** and **1b** in the gas phase, which has been established by the electron diffraction method. It is seen that the S—S bond length in **3a** is 2.19 Å, which is much longer than the average value for the ordinary S—S bond in organic disulfides (2.048 Å).[30] This could be related to the considerable Coulomb repulsion of two positively charged sulfur atoms (*q*: S(1), 0.09; S(2), 0.74). However, the S—S bond in radical **2a** (2.14 Å) is not much shorter, although the sulfur atoms are virtually uncharged (*q* = 0.02 for both). It cannot be excluded that the elongation of the S—S bond is due to the substantial strain of the five-membered heterocycle.

The results on the SN bond lengths in **3a** are of greatest interest. The double S(2)=N(3) bond length in

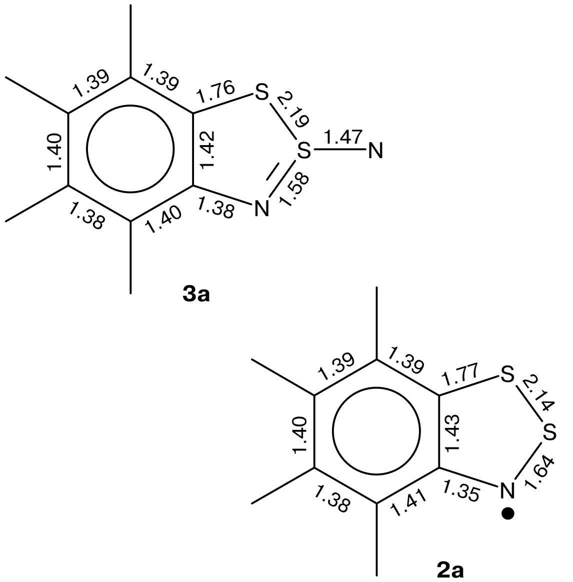
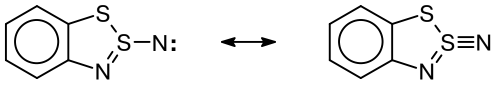


Fig. 7. Some bond lengths (Å) of nitrenoid **3a** and radical **2a** according to B3LYP/6-31G* calculations.

the heterocycle (1.58 Å) is quite typical[1—3,5,6,30] but the length of the exocyclic SN bond (1.47 Å) is much closer to the value for the triple[31—34] than for the ordinary[30] SN bond. So, in thiazyl fluorides FS≡N and $F_3S≡N$ the SN bond length, according to the data of microwave spectroscopy, is equal to 1.448 and 1.416 Å, respectively,[31,32] whereas in the thiazylamide anions R—N—S≡N (R = Ar, Alk), according to X-ray diffraction analysis, it ranges from 1.442 to 1.490 Å.[33,34] These results imply that intermediate **3a** is a nitrenoid species with the structure intermediate between nitrene RS—N**:** and thiazyl RS≡N. (Detailed *ab initio* calculations of the chemical bond structure in intermediate **3a** will be presented elsewhere.)



Thus, precursors of 1,2,3-benzodithiazolyl radicals **2** during the photolysis of 1,3,2,4-benzodithiadiazines **1** are nitrenoid species **3** with the structure intermediate between the structures of 1,2,3-benzodithiazol-2-yl-nitrene and corresponding thiazyl. In order to reveal the routes of the transformation of nitrenoids **3** into radicals **2**, we are performing experiments on laser flash photolysis of compounds **1** and on an analysis of the transformation products of **1** in the presence of typical traps of nitrenes. Note that the possibility of isomerization to **3** explains the ability of compounds **1** to oxidative imination of P^{III} and S^{II} atoms.[6,8]

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