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Preparation of 1,5-dinitrenonaphthalene in cryogenic matrices†

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1,5-Dinitrenonaphthalene was prepared in two cryogenic matrices by photolysis of 1,5-diazidonaphthalene; the cryogenic matrices were an argon matrix at 11 K and a glassy 2-methyltetrahydrofuran matrix at 77 K; the photolysis was analyzed by UV-VIS, FT-IR, and ESR matrix isolation spectroscopies.

Dinitrenes have been intensively studied to examine the magnetic properties of the building blocks in molecule-based magnetic materials.[1] The two nitreno groups in dinitrenes are triplet centers and provide important insight into intramolecular interelectronic exchange interaction. Some dinitrenes exist in the quinonoidal form, where, for each nitreno group, one of the unpaired electrons of the nitrogen atom forms a π bond with a π electron of the adjacent carbon atom.[2,3] Hence, these dinitrenes are not high-spin molecules but diradicals with two localized electrons in a singlet ground state. Even though they are not very attractive as organic magnetic materials for technical applications, these dinitrenes are important species for the study of interelectronic interaction in organic diradicals.[4] In these quinonoidal dinitrenes, electronic interaction between the radical centers is explained by spin polarization,[2] an important interelectronic exchange mechanism. The quinonoidal dinitrenes have been studied to understand the relationship between their interelectronic exchange interaction and their chemical structure.[1] However, frequently there are complicating structural ambiguities, such as twisting of the aromatic system in biphenyl[5,6] or *E*–*Z* iosmerization in stilbene.[2] Connecting two nitreno groups to a condensed polycyclic aromatic hydrocarbon, where structural ambiguity is excluded, should make it easier to study the relationship between structure and interelectronic interaction and could lead to a clearer understanding of this relationship, Here, we studied 1,5-dinitrenonaphthalene, where two nitreno groups were connected to a rigid naphthalene structure, by low temperature matrix isolation spectroscopies.

Crystallites of 1,5-diazidonaphthalene **1** were vaporized at 45 °C and codeposited with argon (99.9999%) onto a CsI plate at 11 K. Matrix-isolated **1**, which showed structured UV-VIS absorption bands in the 300–340 nm region (Fig. 1) and major IR bands at 2116, 1409, 1294, 781, and 707 cm^{-1}, was photolyzed by XeCl excimer laser pulses (λ = 308 nm, 1 Hz, 1.2 mJ cm^{-2} pulse^{-1}, τ = 20 ns). The photolysis was simultaneously monitored by FT-IR and UV-VIS spectroscopies.[7] Upon irradiation at 308 nm, the UV-VIS and IR absorption bands ascribed to **1** decreased rapidly, while some new bands appeared. These new bands behaved differently during irradiation: in the UV-VIS absorption spectra, the weak absorption bands at 581, 565, 541, 535, 391, and 372 nm disappeared after prolonged irradiation, while the absorption bands at 470, 442, and 415 nm increased continuously during the irradiation (Fig. 1). A similar behavior was observed in the FT-IR spectra, with some new bands disappearing and others growing continuously during irradiation. The former bands were ascribed to mononitrene **2** in the triplet state, showing good agreement with the theoretical IR spectrum calculated at the UB3LYP/6-31G* level.† Meanwhile, the FT-IR spectrum obtained upon irradiation with 330 shots (Fig. 2(a)) did not contain the characteristic IR band of the azido group (2116 cm^{-1}). Thus, the resulting product was formed by elimination of two nitrogen molecules from **1** (Scheme 1). This product (**3**) showed a prominent IR band at 750 cm^{-1} and others at 507, 1033, 1161, 1212, 1279, 1393, 1466, and 1506 cm^{-1}. These bands were ascribed to a single photoproduct from the dynamic behavior in intensity during irradiation.[8] Moreover, the dynamic behavior of the IR spectra corresponded to that of the

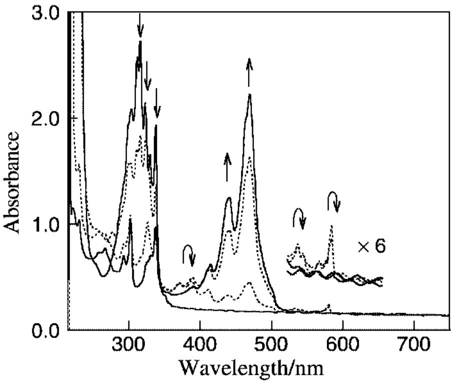


Fig. 1 UV-VIS absorption spectra of **1** photolyzed by XeCl excimer laser pulses (0, 30, 140, and 3440 shots) in an argon matrix. Arrows show the dynamic behavior in intensity of peaks during irradiation.

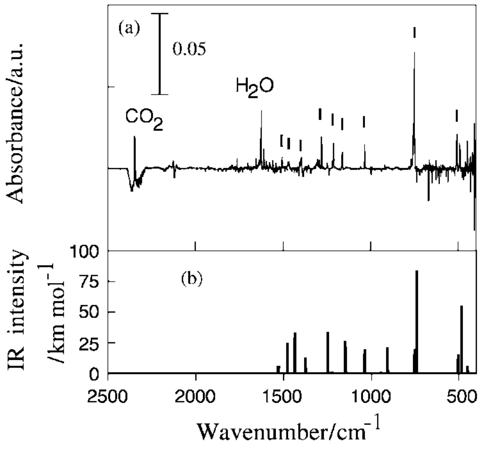
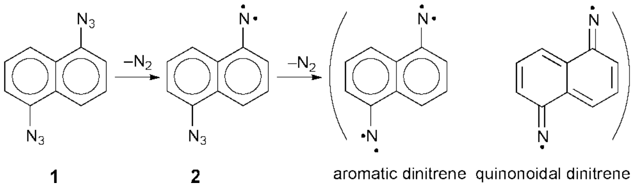


Fig. 2 (a) FT-IR spectrum observed upon irradiation with 330 shots and (b) theoretical IR spectrum of **3** (open-shell singlet state).



Scheme 1

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† Electronic supplementary information (ESI) available: experimental details and computational study of the dinitrenes. See http://www.rsc.org/suppdata/cc/b0/b008560j/

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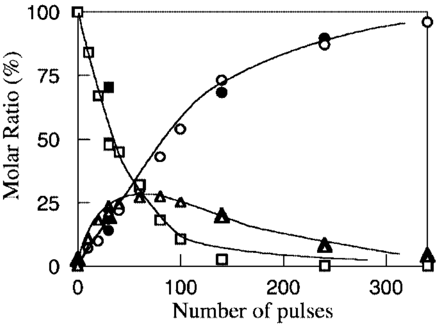

Fig. 3 Dynamic behavior of the intensities in the UV-VIS and FT-IR bands ascribed to **1** (solid squares, 339 nm; open squares, 1409 cm^{-1}), **2** (solid triangles, 581 nm; open triangles, 769 cm^{-1}), and **3** (solid circles, 470 nm; open circles: 750 cm^{-1}).

UV-VIS spectra during the whole irradiation as shown in Fig. 3. This behavior of the UV-VIS and IR bands ascribed to **1**, **2**, and **3** revealed a typical consecutive reaction, that is, consecutive elimination of two nitrogen molecules from **1**.[9] No IR bands ascribable to other species were observed under the present conditions. The observed FT-IR spectrum was compared with the theoretical IR spectrum of 1,5-dinitrenonaphthalene. For the quinonoidal dinitrenes reported as far, the ground state is the singlet diradical state which lies slightly below the triplet state: their energy gaps between singlet and triplet states ($\Delta E_{\text{S-T}}$) are rather small (< 1 kcal mol^{-1}).[2,3] The state order of the dinitrene with different spin multiplicities was often difficult to reproduce in the computational study,[10] since the theoretical calculations for singlet-diradicals show much difficulty because of their multireference character. It has recently been reported that calculations using the symmetry-broken spin-unrestricted DFT method give reasonable solutions for such diradicals.[10–12] Moreover, this method can afford reasonable solutions even for larger molecules. Therefore, preliminary calculations for the singlet, triplet, and quintet states of **3** were carried out at the UB3LYP/6-31G* level. Fig. 2(b) shows the theoretical IR spectrum of the singlet state. The theoretical calculation underestimated the wavenumbers of the IR bands by ~125 cm^{-1}. The deviation was larger than that shown normally in the calculations at this computational level. The deviations would be due to the spin contamination: the results on **3** showed the spin squared expectation ($\langle S^2 \rangle$) value of 1.78, indicating the admixture of the triplet and quintet states. In the symmetry-broken spin-unrestricted calculations, the $\langle S^2 \rangle$ value of the singlet diradical should be 1.0.[11] Although deviations in wavenumber were shown, the observed spectral feature was well described by comparison of those with other spin multiplicities (see ESI†). Moreover, the observed UV-VIS spectra indicated the quinonoidal structure as followed. (1) The UV-VIS bands (470, 442, and 415 nm) of **3** corresponded to that of the 1,5-naphthoquinone derivative (475 and 458 nm) which should have a similar electronic structure to the quinonoidal dinitrene.[13] (2) The INDO/S computation[14] based on the quinonidal geometry of singlet diradical predicts major UV-VIS bands at 468 and 460 nm, that are in agreement with the experimental results. Thus, it is concluded that the photoproduct prepared from **1** was 1,5-dinitrenonaphthalene, which was the quinonoidal singlet diradical in the ground state. The dinitrene **3** was formed by elimination of two nitrogen molecules from **1** without the rearrangement observed for 1- or 2-azidonaphthalenes.[15]

UV-VIS spectroscopy revealed that a similar photolysis occurred for **1** in a glassy 2-methyltetrahydrofuran (MTHF) matrix at 77 K upon a Xe lamp irradiation through a band-pass glass filter ($350 < \lambda < 380$ nm). Under these conditions, ESR spectroscopy (X band) was used to analyze the photolysis of a MTHF solution of **1** (4.6 mM). Upon irradiation, ESR signals at 622 and 611 mT, ascribed to triplet mononitrenes,[16] were observed in addition to the typical impurity signal in the $g = 2$ region. Signals ascribable to a dinitrene with higher spin multiplicity were not observed. The absence of the signals indicated that the ground state of **3** was a singlet diradical. Minato and Lahti[2] and Nimura and others[3] report that 1,4-dinitrenobenzene **4** and several other quinonoidal dinitrenes show ESR signals ascribable to thermally populated excited triplet states. The reason for the absence of such signals can be explained as follows: since 1,5-dinitrenonaphthalene has a larger $\Delta E_{\text{S-T}}$ than **4** and the other quinonoidal dinitrenes, the population of the thermally-excited triplet state is too low to detect. The DFT calculations support our interpretation of the reason why the quinonoidal triplet ESR signals are difficult to detect.† Moreover, theoretical calculations with higher levels by Serwinski *et al.* also support our interpretation.[17]

In conclusion, 1,5-dinitrenonaphthalene was formed by the consecutive elimination of nitrogen molecules from 1,5-diazidonaphthalene upon irradiation at 308 nm in low-temperature matrices. On the basis of matrix isolation spectroscopies and theoretical calculations, we confirmed that the dinitrene formed was a quinonoidal singlet diradical with a relatively large $\Delta E_{\text{S-T}}$. Further study on other dinitrenonaphthalenes is in progress.

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Notes and references

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7 The sample chamber has two pairs of windows: KBr windows for IR measurement and quartz windows for UV-VIS measurement. Therefore, UV-VIS and FT-IR spectra of the same sample matrix can be simultaneously observed.

8 The photoproduct **3** was generated upon irradiation at 308 nm and photolyzed at 248 nm. The dynamic behavior of these bands was analyzed for its generation and decomposition. All of these bands showed similar dynamic behavior.

9 The dynamic behavior in absorbance was scaled to express the molar ratio in the matrix. The molar ratios (%) of **1** and **2** to initial **1** were estimated from the absorbance of the IR bands due to the azido groups in each compound on the basis of their theoretical IR intensities (1929 and 923 km mol^{-1} for **1** and **2**, respectively). The residual portion was allocated to **3** because no other species was detected under the present conditions. The absorbance of the UV-VIS bands are scaled to fit the dynamics in absorbance of the IR bands.

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16 The signal was observed at 622 mT initially, which was ascribed to **2**; this signal corresponds to a zero field splitting of $|D/hc| = 0.918$ cm^{-1}. This signal decreased upon irradiation, while the signal at 611 mT increased. The latter signal was ascribed to 1-amino-5-nitrenonaphthalene by the literature (T. Harder, J. Bendig and G. Sholz, *J. Am. Chem. Soc.*, 1996, **118**, 2497).

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