

## Communication

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Ruijuan Feng, Yan Lu, Guohai Deng, Jian Xu, Zhuang Wu, Hongmin Li, Qian Liu, Norito Kadowaki, Manabu Abe, and Xiaoqing Zeng

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# Magnetically Bistable Nitrenes: Matrix-Isolation of FuroyInitrenes in Both Singlet and Triplet States and Triplet 3-FuryInitrene

Ruijuan Feng,<sup>†</sup> Yan Lu,<sup>†</sup> Guohai Deng,<sup>†</sup> Jian Xu,<sup>†</sup> Zhuang Wu,<sup>†</sup> Hongmin Li,<sup>†</sup> Qian Liu,<sup>†</sup> Norito Kadowaki,<sup>‡</sup> Manabu Abe<sup>‡</sup> and Xiaoqing Zeng<sup>\*,†</sup>

<sup>†</sup>College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China. <sup>‡</sup>Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima Hiroshima 739-8526, Japan.

Supporting Information Placeholder

**ABSTRACT:** Two simple acylnitrenes, 2-furoylnitrene (2) and 3-furoylnitrene (6), were generated through 266 nm laser photolysis of the corresponding azides. Both are magnetically bistable in cryogenic matrices, as evidenced by the direct observation of the closed-shell singlet state with IR spectroscopy in solid Ne, Ar, Kr, Xe, and N<sub>2</sub> matrices (3–40 K) and the triplet state in toluene (10 K) with EPR spectroscopy (<sup>3</sup>2: |D/hc| = 1.48 cm<sup>-1</sup> and |E/hc| = 0.029 cm<sup>-1</sup>; <sup>3</sup>6: |D/hc| = 1.39 cm<sup>-1</sup> and |E/hc|c = 0.039 cm<sup>-1</sup>). Subsequent visible-light and UV laser irradiations led to the formation of furyl isocyanates (3 and 7) and ring-opening product 3-cyanoacrolein (9-*E* and 9-*Z*), respectively, in which the elusive 3-furylnitrene (<sup>3</sup>8) was also identified by IR and EPR spectroscopy (|D/hc| = 1.12 cm<sup>-1</sup> and |E/hc| = 0.005 cm<sup>-1</sup>).

Nitrenes are versatile reactive intermediates in chemical transformations such as aziridination and C-H amidation reactions.<sup>1</sup> Meanwhile, nitrenes have been broadly used in the functionalization of carbon-nanomaterials<sup>2</sup> and photoaffinity labeling of biological systems.<sup>3</sup> As the most fundamental property of nitrenes, electronic spin state determines the structure and reactivity. Generally, nitrenes prefer triplet ground state in which the two unpaired electrons have parallel spins, singly occupying pure  $p_x$  and  $p_z$  orbitals. Whereas, singlet state with antiparallel spin is less favorable due to much stronger Coulombic electron-electron repulsion.<sup>4</sup> The singlet-triplet energy gaps ( $\Delta E_{ST}$ ) in nitrenes depend strongly on the substituents. For instance, delocalization of unpaired electron by conjugation in vinylnitrenes<sup>5</sup> and arylnitrenes<sup>6</sup> can stabilize the singlet state relative to the triplet ground state with reduced  $\Delta E_{ST}$ .

Stabilization of the singlet state has also been proposed for acylnitrenes (RC(O)N),<sup>4</sup> which is due to bonding interaction between the carbonyl oxygen (C=O) and the electron-deficient nitrene center (II, III, Scheme 1). This intramolecular interaction results in closed-shell singlet state with a cyclic oxazirine-like structure (III). Experimentally, ultrafast spectroscopy, matrixisolation spectroscopy, and electron paramagnetic resonance spectroscopy (EPR) have confirmed singlet ground state ( $\Delta E_{ST} < 0$ kcal mol<sup>-1</sup>) for aroylnitrenes such as benzoylnitrene (PhC(O)N)<sup>7</sup> and naphthoylnitrene (2-NpC(O)N),<sup>8</sup> the higher-energy triplet state (I, Scheme 1) could only be detected as transient species by ultrafast spectroscopy. Meanwhile, many acylnitrenes such as alkoxynitrenes (RO-C(O)N)<sup>9</sup> and carbamoylnitrenes (R<sub>2</sub>N-C(O)N)<sup>10</sup> adopt triplet multiplicity ( $\Delta E_{ST} > 0$  kcal mol<sup>-1</sup>).



Scheme 1. Structures of acylnitrenes

Therefore, fundamentally important simple acylnitrenes with almost degenerate singlet and triplet states ( $\Delta E_{\rm ST} \approx 0$  kcal mol<sup>-1</sup>) should be viable candidates for isolation and characterization. Very recently, arylcarbenes with small magnitude of  $\Delta E_{\rm ST}$  have been observed in their both singlet and triplet states in cryogenic matrices.<sup>11</sup> It was concluded that the magnetic bistability of carbenes should be a general phenomenon that solely depends on the singlet-triplet gap  $\Delta E_{\rm ST}$ . Continuing our interest in the structure and reactivity of  $\alpha$ -oxo nitrenes,<sup>12</sup> herein, we report the photochemistry of two furoylazides (1 and 5), in which furoylnitrenes (2 and 6), featuring as rare magnetically bistable nitrenes, and the elusive 3-furylnitrene (8) have been isolated and characterized in cryogenic matrices.



Scheme 2. Photochemistry of furoylazides.

Prior to the experimental study, the  $\Delta E_{\rm ST}$  values for furoylnitrenes together with HC(O)N<sup>13</sup> and PhC(O)N<sup>7,8</sup> were calculated (Table 1). Although the B3LYP/6-311++G(3df,3pd) method is adequate for the prediction of IR spectra, it tends to underestimate the stability of the singlet relative to the triplet for  $\pi$ -conjugated systems

due to overemphasis of delocalization.<sup>14</sup> In consistent with previous studies,<sup>7,8,13</sup> the CCSD(T)/aug-cc-pVTZ and CBS-QB3 methods conclusively predict the preference of triplet and singlet state for the last two nitrenes, respectively. However, for both furoylnitrenes the sign of the calculated small  $\Delta E_{\rm ST}$  values varies with the computational methods, indicating that the two spin states are almost equal in energy. For all four acylnitrenes, single-point energy calculations using the complete-active-space second-order perturbation theory (CASPT2) predicted preference of the triplet state, and the open-shell singlet are significantly higher by more than 25 kcal mol<sup>-1</sup> (Table S1).

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Table 1. Calculated  $\Delta E_{\rm ST}$  (kcal mol<sup>-1</sup>) for acylnitrenes

species	B3LYP <sup>[a]</sup>	CCSD(T) <sup>[b]</sup>	CBS-QB3	CASPT2
HC(O)N	8.3	2.2	0.7	4.9 <sup>[d]</sup>
PhC(O)N	4.6	-0.4	-4.7	1.1 <sup>[e]</sup>
<b>2</b> <sup>[c]</sup>	6.5	1.2	-1.2	2.6 <sup>[f]</sup>
<b>6</b> <sup>[c]</sup>	5.8	0.8	-1.1	2.2 <sup>[f]</sup>

[a] At the 6-311++G(3df,3pd) basis set. [b] CCSD(T)/aug-ccpVTZ//B3LYP/6-311++G(3df,3pd). [c] For the more stable conformers of the two states. [d] CASPT2(4,3)/ccpVTZ//CASSCF(6,5)/cc-pVTZ. [e] CASPT2(12,11)/ccpVTZ//CASSCF(12,11)/cc-pVTZ. [f] CASPT2(12,10)/ccpVTZ//CASSCF(12,10)/cc-pVTZ. Positive values refer to the triplet being more stable.

The generation of 2-furoylnitrene (2) was performed by 266 nm laser photolysis (10 mW, 30 s) of 2-furoylazide (1) in solid Ne matrix (3 K). The IR difference spectrum (Figure 1A) shows the depletion of the azide (ca. 80%) and the concomitant formation of N<sub>2</sub> (IR inactive) and the Curtius-rearrangement product 2-furylisocyanate (3, Table S2), the latter exhibits intense IR band for the characteristic NCO asymmetric stretching vibration at 2278.6 cm<sup>-1</sup> with a shift of 12.5 cm<sup>-1</sup> upon <sup>15</sup>N labeling. Reference IR spectrum of 3 can be readily obtained since flash pyrolysis of 1 at 500 K exclusively furnishes 3 and N<sub>2</sub> (Figure S1).



Figure 1. A) IR difference spectrum showing the decomposition of 1 (bands pointing downward) in Ne matrix (3 K) upon a 266 nm laser irradiation; B) IR difference spectrum (5 times expanded along the  $\Delta A$  axis) showing rearrangement of 2 to 3 upon subsequent visible light irradiation (440±20 nm), bands of impurity H<sub>2</sub>O (\*) are marked; C-D) B3LYP/6-311++G(3df,3pd) calculated

IR spectra (unscaled harmonic frequencies) of  $anti-{}^{1}2$  and  $syn-{}^{3}2$ , respectively.

Several new IR bands appeared at around 1760 cm<sup>-1</sup>, and the corresponding carrier can be completely depleted by blue light irradiation (440±20 nm, 40 min), as a result 3 and traces of the azide precursor 1 were formed (Figure 1B). To aid the assignment, IR frequency calculations (B3LYP/6-311++G(3df,3pd)) of the most likely candidate 2-furoylnitrene (2) were performed. The band centered at 1752.3 cm<sup>-1</sup> coincides with the calculation of 1818 cm<sup>-1</sup> for the singlet nitrene (Figure 1C) in a more favorable anti conformation (syn conformer: 1807 cm<sup>-1</sup>, Table S3). The frequency is very close to the most characteristic C=N stretching vibrations found in other oxazirine-like singlet aroylnitrenes such as PhC(O)N (1760 cm<sup>-1</sup> in CD<sub>3</sub>CN)<sup>7a-b</sup> and 2-NpC(O)N (1737 cm<sup>-1</sup> in CCl<sub>4</sub>).<sup>8</sup> The assignment is supported by the observation of an isotopic shift of 8.5 cm<sup>-1</sup> upon <sup>15</sup>N-labeling (Figure S2). Interestingly, there are several weaker bands in the range of 1800-1730 cm<sup>-1</sup>, all of which exhibit same photobehavior and also same <sup>15</sup>N isotopic shift. These bands appear with minor shifts ( $< 10 \text{ cm}^{-1}$ ) and slightly changed intensities in independent experiments where N<sub>2</sub> was used as the matrix gas at 15 K (Figure S3). Hence, they also belong to the nitrene  $^{1}2$ , and the splittings might be caused by weak interaction with the surrounding molecules in same matrix cages (matrix site effect).<sup>1</sup>

The selective depletion of <sup>1</sup>2 allows unambiguous identification of the remaining IR bands and <sup>15</sup>N isotopic shifts (Table S3). No distinguishable IR band could be found for triplet 2-furoylnitrene, especially for the most characteristic C=O stretching vibrations which were predicted at 1603 (*anti*) and 1611 cm<sup>-1</sup> (*syn*) with large IR intensities (*anti*: 127 km mol<sup>-1</sup>; *syn*: 201 km mol<sup>-1</sup>). Typically, matrix-isolated triplet acylnitrenes like CH<sub>3</sub>OC(O)N (*syn*: 1645.8 cm<sup>-1</sup>; *anti*: 1602.8 cm<sup>-1</sup>)<sup>9b</sup> and H<sub>2</sub>NC(O)N (1644.4 cm<sup>-1</sup>)<sup>10</sup> display intense bands for this IR fundamental.

The generation of singlet 3-furoylnitrene  $(^{1}6)$  through 266 nm laser photolysis of 3-furoylazide (5) was also observed (Figure 2A).



Figure 2. A) IR difference spectrum showing the decomposition of 5 (bands pointing downward) in Ne matrix (3 K) upon a 266 nm laser irradiation; B) IR difference spectrum (5 times expanded along the  $\Delta A$  axis) showing rearrangement of 6 to 7 upon subsequent UV light irradiation (365 nm); C-D) B3LYP/6-311++G(3df,3pd) calculated IR spectra (unscaled harmonic frequencies) of *anti*-<sup>1</sup>6 and *syn*-<sup>3</sup>6, respectively.

As can be seen in Figure 2B, <sup>1</sup>6 exhibits IR bands at 1786.0 and 1764.2 cm<sup>-1</sup> for the C=N stretching vibration (1781.3 and 1762.3 cm<sup>-1</sup> in N<sub>2</sub>-matrix, Figure S4), and the corresponding <sup>15</sup>N isotopic shifts are 10.1 and 8.2 cm<sup>-1</sup> (Figure S5), respectively. The remain-

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ing bands (> 600 cm<sup>-1</sup>) show good agreement with the calculations for the nitrene in the singlet state (Figure 2C). Subsequent UV light (365 nm) irradiation leads to the expected rearrangement to isocyanate 7. In order to convert the singlet furoylnitrenes to the triplet state, attempts were made by warming the matrices (N<sub>2</sub>matrix to 25 K and Kr-matrix to 40 K, Figures S6-S7), doping the matrix with 1% water (Figures S8-S9) or carbon monoxide (Figures S10), or irradiating with longer-wavelength light sources (570 and 830 nm), however, only the rearrangement occurred in the case of irradiations.

Given the possibility that the absence of distinguishable IR bands for triplet furoylnitrenes might be due to low abundances in cryogenic matrices, the photochemistry (266 nm) of 2-furoylazide in solid Ar (10 K) was followed by EPR spectroscopy. No EPR signals for triplet species were observed. However, when the photolysis was performed in polar solvent toluene (10 K), typical EPR signals for triplet nitrenes appeared after 2 min of irradiation (Figure 3). These signals are persistent at 10 K in the dark at least for 11 hours but disappear when warming the matrix to 50 K (Figure S11), however, subsequent recooling the matrix to 10 K could not recover the signals. Two sets of zero-field splitting (zfs) parameters  $|D/hc| = 1.48 \text{ cm}^{-1}$  and  $|E/hc| = 0.029 \text{ cm}^{-1}$  and |D/hc| = 1.39 $cm^{-1}$  and  $|E/hc| = 0.039 cm^{-1}$  are close to those of acylnitrenes like CH<sub>3</sub>OC(O)N ( $|D/hc| = 1.66 \text{ cm}^{-1}$  and  $|E/hc| = 0.020 \text{ cm}^{-1}$ )<sup>9b</sup> and  $H_2NC(O)N(|D/hc| = 1.59 \text{ cm}^{-1} \text{ and } |E/hc| = 0.018 \text{ cm}^{-1}),^{16} \text{ demon-}$ strating the presence of triplet furoylnitrene nitrenes. The observed D values agree with the predictions  $(syn^{-3}2: 1.40 \text{ cm}^{-1}, syn^{-1})$ <sup>3</sup>6: 1.40 cm<sup>-1</sup>) by the empirical linear correlation ( $D = 1.96673\rho$  – 2.0557 cm<sup>-1</sup>) with the calculated natural spin densities  $\rho$  (syn-<sup>3</sup>2: 1.756, syn-<sup>3</sup>6: 1.755, B3LYP/EPRIII).<sup>1a,17</sup>



**Figure 3.** A) EPR spectrum ( $v_0 = 9.3963$  GHz) showing generation of <sup>3</sup>**2** (zfs parameters: |D/hc| = 1.48 cm<sup>-1</sup> and |E/hc| = 0.029 cm<sup>-1</sup>) during the photolysis (266 nm, 10 min) of **1** in solid toluene at 10 K; B) EPR spectrum ( $v_0 = 9.3989$  GHz) showing the generation of <sup>3</sup>**6** (|D/hc| = 1.39 cm<sup>-1</sup> and |E/hc| = 0.039 cm<sup>-1</sup>) and <sup>3</sup>**8** (|D/hc| = 1.12 cm<sup>-1</sup> and |E/hc| = 0.005 cm<sup>-1</sup>) during the photolysis (266 nm, 5 min) of **5** in solid toluene at 10 K.

Additionally, a second triplet nitrene signal appeared during the photolysis of **5**. The parameters  $|D/hc| = 1.12 \text{ cm}^{-1}$  and  $|E/hc| = 0.005 \text{ cm}^{-1}$  imply the presence of an arylnitrene, for which usually small zfs parameters were observed, such as phenylnitrene  $(|D/hc| = 0.9896 \text{ cm}^{-1} \text{ and } |E/hc| = 0.00 \text{ cm}^{-1})^{18}$  and 2-pyrimidinylnitrene  $(|D/hc| = 1.217 \text{ cm}^{-1} \text{ and } |E/hc| = 0.0052 \text{ cm}^{-1})^{.19}$  Considering the frequently observed CO-elimination in covalent isocyanates, <sup>96,10</sup> this signal is very likely to be associated with 3-furylnitrene (<sup>3</sup>8), formed from CO-elimination in **7**. Instead, 2-furylnitrene (**4**) was not observed in the laser photolysis of 2-furoylazide (**1**). The ob-

servation is consistent with the theoretical prediction that the optimization of **4** in the initially generated singlet state led directly to the ring-opened cyanoacrolein (**9**, Figure S12).<sup>20</sup>

To verify the formation of  ${}^{3}8$ , a Ne-matrix mainly containing 7 was irradiated with an ArF excimer laser (193 nm). The resulting IR difference spectrum (Figure 4A) reflects the formation of CO and new species with several weak IR bands, which can be distinguished by subsequent purple light irradiation (400±20 nm), under which 9 forms at the expense of  ${}^{3}8$  (Figure 4B). The assignment was affirmed by comparing with the calculated spectrum of 8 (Figure 4C) and also the <sup>15</sup>N-labeling experiment (Figure S13). In line with the observation with EPR spectroscopy, only 9 was observed by IR spectroscopy when 3 was subjected to the UV laser irradiation. Furthermore, the visible light (400±20 nm) induced  $Z \rightarrow E$  conformational conversion in 9 was observed (Figure S14). The ring-opening of furylnitrenes (Figure S12) resembles the recently disclosed photochemistry of the putative isoelectronic furylcarbenes,<sup>21</sup> which were proposed as the intermediates in the photolysis of furyldiazomethanes.



**Figure 4.** A) IR difference spectrum showing the decomposition of **5** and **7** in Ne matrix (3 K) upon 193 nm laser irradiation; B) IR difference spectrum (20 times expanded along the  $\Delta 4$  axis) showing the rearrangement of <sup>3</sup>**8** to **9** in Z and *E* conformations upon subsequent purple light irradiation (400±20 nm); C-D) B3LYP/6-311++G(3df,3pd) calculated IR spectra (unscaled harmonic frequencies) of triplet and singlet **8**, respectively.

In conclusion, two novel furoylnitrenes (2 and 6) have been generated from 266 nm laser photolysis of the corresponding azide precursors. In consistent with the theoretically predicted small singlet-triplet energy gaps ( $\Delta E_{\rm ST} \approx 0$  kcal mol<sup>-1</sup>), subsequent characterization by IR and EPR spectroscopy demonstrates that both nitrenes exist as persistent species in the closed-shell singlet and triplet states in cryogenic matrices. Upon near-visible light irradiations, furoylnitrenes rearrange to furylisocyanates, which further dissociate into CO and 3-cyanoacrolein via the intermediacy of intriguing furylnitrenes. No evidence for the thermally initiated switch of spin state in furoylnitrenes was obtained. The reason might be due to intrinsic barriers (9-10 kcal mol<sup>-1</sup>, B3LYP/6-311++G(3df,3pd)) associated with the structural changes (Figures S15-S24) in the course of intersystem crossing (ISC), which could hardly be reached by warming the matrix in the available temperature range (up to 40 K). More importantly, these barriers are close to those (10–11 kcal mol<sup>-1</sup>) for the rearrangement of the singlet furoylnitrenes to the isocyanates, which is thermodynamically much more favorable due to the concomitant release of large amount of energy (>70 kcal  $mol^{-1}$ ). Work in our group is ongoing to replace the furyl group with other aryl substituents, in the hope of discovering heteroaroylnitrenes with thermally and/or photolytically switchable spin states in cryogenic matrices.

### ASSOCIATED CONTENT

### Supporting Information

Experimental details, theoretical methods, observed and calculated IR spectra, and calculated energies and atomic coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

# 10<br/>11AUTHOR INFORMATION

### Corresponding Author

\*xqzeng@suda.edu.cn

#### Notes

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The authors declare no competing financial interests.

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### REFERENCES

For very recent reviews, see: (a) Wentrup, C. Chem. Rev. 2017, 117, 4562–4623. (b) Park, Y.; Kim, Y.; Chang, S. Chem. Rev. 2017, 117, 9247–9301.

(2) Park, J. Yan, M. Acc. Chem. Res. 2013, 46, 181–189, and references therein.

31 (3) For examples, see: (a) Panov, M. S.; Voskresenska, V. D.; Ryazantsev,
32 M. N.; Tarnovsky, A. N.; Wilson, R. M. J. Am. Chem. Soc. 2013, 135, 19167–19179. (b) Gritsan, N. P.; Platz, M. S. Chem. Rev. 2006, 106, 3844–3867.

- (4) For examples, see: (a) Falvey, D. E.; Gudmundsdottir, A. D. Nitrenes and Nitrenium Ions; Wiley: New York, 2013. (b) Gritsan, N. P.; Platz, M. S.; Borden, W. T. The Study of Nitrenes by Theoretical Methods in Theoretical Methods in Photochemistry; Kutateladze, A., Ed.; Taylor and Francis: Boca Raton, FL, 2005. (c) Reactive Intermediate Chemistry; Moss, R. A., Platz, M. S., Jones, M. J., Jr., Eds.; John Wiley & Sons: Hoboken, NJ, 2004. (d) Barbieux-Flammang, M.; Vandevoorde, S.; Flammang, R.; Wong, M. W.; Bibas, H.; Kennard, C. H. L.; Wentrup, C. J. Chem. Soc.,
- 40 Perkin Trans. 2, 2000, 473–478.
  41 (5) (a) Sarkar, S. K.; Osisioma, O.; Karney, W. L.; Abe, M.; Gud-mundsdottir, A. D. J. Am. Chem. Soc. 2016, 138, 14905–14914. (b) Sarkar, S. K.; Sawai, A.; Kanahara, K.; Wentrup, C.; Abe, M.; Gud-mundsdottir, A. D. J. Am. Chem. Soc. 2015, 137, 4207–4214.
- (6) (a) Kvaskoff, D.; Lüerssen, H.; Bednarek, P.; Wentrup, C. J. Am. *Chem. Soc.* 2014, *136*, 15203–15214. (b) Borden, W. T.; Gritsan, N. P.;

Hadad, C. M. Karney, W. L.; Kemnitz, C. R.; Platz, M. S. Acc. Chem. Res.
2000, 33, 765–771. (c) Nues, C. M.; Knezz, S. N.; Reva, I.; Fausto, R.;
McMahon, R. J. J. Am. Chem. Soc. 2016, 138, 15287–15290. (d) Rau, N.
J.; Welles, E. A.; Wenthold, P. G. J. Am. Chem. Soc. 2013, 135, 683–690.
(7) (a) Pritchina, E. A.; Gritsan, N. P.; Maltsev, A.; Bally, T.; Autrey, T.;
Liu, Y. L.; Wang, Y. H.; Toscano, J. P. Phys. Chem. Chem. Phys. 2003, 5, 1010–1018. (b) Desikan, V.; Liu, Y. L.; Toscano, J. P.; Jenks, W. S. J.
Org. Chem. 2007, 72, 6848–6859. (c) Wentrup, C.; Bornemann, H. Eur. J.
Org. Chem. 2005, 4521–4524. (d) Wasserman, E.; Smolinsky, G.; Yager, W. A. J. Am. Chem. Soc. 1964, 86, 3166–3167.

(8) (a) Kubicki, J.; Zhang, Y.; Vyas, S.; Burdzinski, G.; Luk, H. L.; Wang, J.; Xue, J.; Peng, H. -L.; Pritchina, E. A.; Sliwa, M.; Buntinx, G.; Gritsan, N. P.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 9751–9761. (b) Kubicki, J.; Zhang, Y.; Wang, J.; Luk, H. L.; Peng, H. -L.; Vyas, S.; Platz, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 4212–4213. (c) Kubicki, J.; Zhang, Y.; Xue, J.; Luk, H. L.; Platz, M. S. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10377–10390.

(9) (a) Chavez, T. A.; Liu, Y.; Toscano, J. P. *J. Org. Chem.* **2016**, *81*, 6320–6328. (b) Li, H. M.; Wu, Z.; Li, D. Q.; Wan, H. B.; Xu, J.; Abe, M.; Zeng, X. Q. Chem. Commun. **2017**, *53*, 4783–4786.

(10) Li, H. M.; Wan, H. B.; Wu, Z.; Li, D. Q.; Bégué, D.; Wentrup, C.; Zeng, X. Q. *Chem. -Eur. J.* **2016**, *22*, 7856–7862, and references therein.

(11) (a) Tsegaw, Y. A.; Kadam, P. E.; Tötsch, N.; Sanchez-Garcia, E.; Sander, W. J. Am. Chem. Soc. 2017, 139, 12310–12316. (b) Costa, P.; Lohmiller, T.; Trosien, I.; Savitsky, A.; Lubitz, W.; Fernandez-Oliva, M.; Sanchez-Garcia, E.; Sander, W. J. Am. Chem. Soc. 2016, 138, 1622–1629.
(c) Henkel, S.; Costa, P.; Klute, L.; Sokkar, P.; Fernandez-Oliva, M.; Thiel, W.; Sanchez-Garcia, E.; Sander, W. J. Am. Chem. Soc. 2016, 138, 1689–1697.

(12) Wu, Z.; Li, D. Q.; Li, H. M.; Zhu, B. F.; Sun, H. L.; Francisco, J. S.;
Zeng, X. Q. Angew. Chem., Int. Ed. 2016, 55, 1507–1510. (b) Deng, G. H.;
Wu, Z.; Li, D. Q.; Linguerri, R.; Francisco, J. S.; Zeng, X. Q. J. Am. Chem. Soc. 2016, 138, 11509–11512.

(13) (a) Mebel, A. M.; Luna, A.; Lin, M. C.; Morokuma, K. J. Chem. Phys. 1996, 105, 6439–6454. (b) Shapley, W. A.; Bacskay, G. B. J. Phys. Chem. A 1999, 103, 6624–6631. (c) Zeng, X. Q.; Bernhardt, E.; Beckers, H.; Banert, K.; Hagedorn, M.; Liu, H. L. Angew. Chem. Int. Ed. 2013, 52, 3503–3506, and references therein.

(14) (a) Perrotta, R. R.; Winter, A. H.; Coldren, W. H.; Falvey, D. E. J. Am. Chem. Soc. 2011, 133, 15553–15558. (b) Woodcock, H. L.; Moran, D.; Brooks, B. R.; Schleyer, P. v. R.; Schaefer, III, H. F. J. Am. Chem. Soc. 2007, 129, 3763–3770.

(15) For a very recent example, see: Schleif, T.; Mieres-Perez, J.; Henkel, S.; Ertelt, M.; Borden, W. T.; Sander, W. *Angew. Chem. Int. Ed.* **2017**, *56*, 10746–10749.

(16) Wan, H. B.; Li, H. M.; Xu, J.; Wu, Z.; Liu, Q. F.; Chu, X. X.; Abe, M.; Bégué, D.; Zeng, X. Q. Org. Chem. Front. **2017**, *4*, 1839–1848.

(17) (a) Kvaskoff, D.; Bednarek, P.; George, L.; Waich, K.; Wentrup, C. J. Org. Chem. 2006, 71, 4049–4058. (b) Wentrup, C.; Kvaskoff, D. Aust. J. Chem. 2013, 66, 286–296.

(18) Kuzaj, M.; Lüerssen, H.; C. Wentrup, Angew. Chem., Int. Ed. 1986, 25, 480-482.

- (19) Torker, S.; Kvaskoff, D.; Wentrup, C. J. Org. Chem. 2014, 79, 1758–1770.
- (20) Wenthold, P. G. J. Org. Chem. 2012, 77, 208-214.
- (21) Pharr, C. R.; Kopff, L. A.; Bennett, B.; Reid, S.; McMahon, R. J. J.
- Am. Chem. Soc. 2012, 134, 6443-6454.







Figure 1. A) IR difference spectrum showing the decomposition of 1 (bands pointing downward) in Ne matrix (3 K) upon a 266 nm laser irradiation; B) IR difference spectrum (5 times expanded along the ΔA axis) showing rearrangement of 2 to 3 upon subsequent visible light irradiation (440±20 nm), bands of impurity H2O (\*) are marked; C-D) B3LYP/6-311++G(3df,3pd) calculated IR spectra (unscaled harmonic frequencies) of anti-12 and syn-32, respectively.

260x188mm (300 x 300 DPI)





Figure 2. A) IR difference spectrum showing the decomposition of 5 (bands pointing downward) in Ne matrix (3 K) upon a 266 nm laser irradiation; B) IR difference spectrum (5 times expanded along the ΔA axis) showing rearrangement of 6 to 7 upon subsequent UV light irradiation (365 nm); C-D) B3LYP/6-311++G(3df,3pd) calculated IR spectra (unscaled harmonic frequencies) of anti-16 and syn-36, respectively.

260x199mm (300 x 300 DPI)





Figure 3. A) EPR spectrum (v0 = 9.3963 GHz) showing generation of 32 (zfs parameters: |D/hc| = 1.48 cm - 1 and |E/hc| = 0.029 cm - 1) during the photolysis (266 nm, 10 min) of 1 in solid toluene at 10 K; B) EPR spectrum (v0 = 9.3989 GHz) showing the generation of 36 (|D/hc| = 1.39 cm - 1 and |E/hc| = 0.039 cm - 1) and 38 (|D/hc| = 1.12 cm - 1 and |E/hc| = 0.005 cm - 1) during the photolysis (266 nm, 5 min) of 5 in solid toluene at 10 K.

260x199mm (300 x 300 DPI)

59 60

57 58



Figure 4. A) IR difference spectrum showing the decomposition of 5 and 7 in Ne matrix (3 K) upon 193 nm laser irradiation; B) IR difference spectrum (20 times expanded along the ΔA axis) showing the rearrangement of 38 to 9 in Z and E conformations upon subsequent purple light irradiation (400±20 nm);
 C-D) B3LYP/6-311++G(3df,3pd) calculated IR spectra (unscaled harmonic frequencies) of triplet and singlet 8, respectively.

260x199mm (300 x 300 DPI)









Graphical abstract

237x139mm (300 x 300 DPI)