Reversible Photoisomerization among Triplet Amino Naphthylnitrene, Triplet Diimine Biradical, and Indazole: Matrix-Isolation IR Spectra of 8-Amino-1-naphthylnitrene, 1,8-Naphthalenediimine, and 1,2-Dihydrobenz[cd]indazole

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S Supporting Information

ABSTRACT: Reaction mechanisms of nitrene, one of the most famous biradicals, have been frequently studied, and many spectral data have been obtained so far. In the present study, the experimental IR spectra of triplet 8-amino-1-naphthylnitrene (³ANN), a triplet diimine biradical 1,8-dihydro-1,8-naphthalenediimine (³DND), and 1,2-dihydrobenz[*cd*]indazole (DBI), which are produced in the UV photolysis of 1,8-diaminonaphthalene in an Ar matrix and identified by a combination method of IR spectroscopy and DFT quantum chemical calculations, are first reported. ³ANN is found to change to DBI by hydrogen-atom migration with bond making between the two nitrogen atoms upon visible-light irradiation ($\lambda > 580$ nm) with its backward reaction caused by 350 nm irradiation. In addition, ³ANN isomerizes to ³DND by 700 nm irradiation, while its backward reaction occurs upon 500 nm irradiation. The wavelength dependences of these photoisomerizations are explained in terms of their electronic transition energies estimated by time-dependent DFT calculations. It is concluded that the novel reversible photoisomerization between phenylnitrene and a seven-membered cyclic compound.



■ INTRODUCTION

Nitrenes are important intermediates in chemical organic reactions, and many researchers have conducted to experimentally identify various nitrenes usually produced by photolysis or pyrolysis of the corresponding azido compounds.^{1–4} One of the simplest nitrene is well-known phenylnitrene, which shows a unique reversible photoisomerization; phenylnitrene changes to azacyclrohepta-1,3,5,6-tetraene, a seven-membered ring compound, by 485 nm irradiation with its backward reaction by 334 nm irradiation.^{5,6} The reversible photoinduced isomerization has been frequently investigated so far,^{7–9} and some analogous systems have been found; for example, 1-naphthylnitrene reversibly isomerizes to the corresponding azirine and a seven-membered cyclic ketenimine.¹⁰ However, besides the above phenylnitrene systems, fewer reversible photoisomerization systems including nitrenes have been reported.^{1,3}

In this study, novel reversible photoinduced isomerization systems among a triplet nitrene, 8-amino-1-naphthylnitrene (³ANN), a triplet biradical, 1,8-dihydro-1,8-naphthalenediimine (³DND), and 1,2-dihydrobenz[*cd*]indazole (DBI) without the corresponding azirine and seven-membered cyclic ketenimine (7-CK) were fortuitously found in the photolysis of 1,8-diaminonaphtharene (DAN) isolated in an Ar matrix, as shown in Scheme 1. One may try to synthesize ³ANN by photolysis of the corresponding azide, 8-amino-1-azidonaphthalene, as a standard photoproduction process, but we happened to find





that ³ANN was produced in the photolysis of DAN upon UV irradiation to yield a new cyclic compound, DBI, in analogous to the photolysis of 1,2-diaminobenzene to yield 5,6-diimino-1,3-cyclohexatriene and 7,8-diazabicyclo[4.2.0]octa-1,3,5-triene.^{11,12} Here, the observed matrix-isolation IR spectra of new three species, ³ANN, ³DND and DBI, are reported, and

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then their photoisomerization mechanisms are discussed based on the experimental results with the aid of time-dependent density functional theory (TD-DFT) calculations.

EXPERIMENTAL AND CALCULATION METHODS

The combination method of matrix-isolation IR spectroscopy with DFT calculation was used. A small amount of DAN (Tokyo Chemical Industry) evaporated at 302 K with excess pure Ar gas was deposited onto a CsI plate at ca. 15 K. All IR spectra of samples isolated in matrices were measured with an FT-IR spectrophotometer (Jeol, JIR-7000); the accumulation number of 100 and the spectral resolution of 0.5 cm⁻¹. A superhigh-pressure mercury lamp was used as a light source to induce photoreactions through some shorter-wavelength cutoff filters. Other experimental details were reported elsewhere.^{11,12} All calculations including optimized structures and predicted IR spectral patterns were performed using unrestricted B3LYP functional with a 6-31++G(d,p) basis set on Gaussian09W.¹³

RESULTS AND DISCUSSION

Upon UV irradiation ($\lambda > 300$ nm) for 15 min, DAN isolated in an Ar matrix multiply yielded chemical species. The measured IR spectrum was slightly complicated as shown in Figure S1 in the Supporting Information, and it was hard to identify the photoproducts clearly. When the matrix sample was exposed to visible light ($\lambda > 580$ nm) for 270 min following the UV preirradiation ($\lambda > 300$ nm), a simple IR spectral change due to the photoconversion of one photoproduct was measured (Figure 1). The measured spectrum of the product in the



Figure 1. (a) Difference spectrum obtained by isomerization from ³ANN to *t*-DBI upon visible-light irradiation ($\lambda > 580$ nm) following the UV preirradiation ($\lambda > 300$ nm). (b) Simulated spectrum composed of the calculated spectral patterns for ³ANN in the downside and *t*-DBI in the upside, obtained at the B3LYP/6-31++G(d,p) level using a scaling factor of 0.98.

upside resembles the calculated spectral pattern of *t*-DBI rather than that of *c*-DBI. The notations of *t* and *c* represent *trans* and *cis* conformations around the N–N bond for the two hydrogen atoms bonded to the nitrogen atoms, respectively. Our DFT calculations showed that *t*-DBI is more stable than *c*-DBI by 23.8 kJ mol⁻¹. The increasing bands at 3339, 763, and 725 cm⁻¹ were assignable to the N–H stretching, the N–H bending and the C–H bending modes of *t*-DBI, respectively, but not of *c*-DBI, (see Figure S2). A comparison of the observed and calculated wavenumbers is shown in Table 1 with their vibrational modes. It is found that most of the observed

Table 1. Observed and Calculated Wavenumbers (in cm^{-1}) of *t*-DBI

| obsd | | calcd ^a | | |
|---------|------|--------------------|------|---------------------------------------|
| ĩ | abs | ĩ | int | assignment ^b |
| 3346 | 2.5 | 3468 | 9.9 | ν (N-H) |
| 3339 | 3.2 | 3463 | 17.1 | ν (N-H) |
| | | 3144 | 12.2 | ν (C-H) |
| | | 3133 | 19.5 | ν (C-H) |
| 1635 | 7.6 | 1639 | 32.7 | $\nu(C-C)$ |
| 1633 | 10.9 | 1629 | 23.5 | $\nu(C-C)$ |
| 1591 | 13.2 | 1601 | 44.0 | $\nu(C-C)$ |
| 1385 | 13.7 | 1388 | 22.1 | ν (C–C) + δ (N–H) |
| 1342 | 0.9 | 1342 | 13.3 | ν (C–C) + δ (N–H) |
| 1328 | 6.9 | 1333 | 8.8 | δ (N-H) |
| 1161 | 7.4 | 1164 | 5.5 | δ (C-H) |
| 1017 | 2.0 | 1014 | 24.5 | $\nu(N-N)$ |
| 849 | 3.3 | 893 | 6.2 | $\delta_{ip}(CCC) + \delta(N-H)$ |
| 841 | 3.9 | 838 | 13.5 | $\delta_{oop}(C-H)$ |
| 823 | 4.2 | 811 | 35.4 | $\nu(ring)$ |
| 809/811 | 15.9 | 798 | 24.1 | $\delta_{ m oop}(m ring)$ |
| 763 | 100 | 776 | 100 | $\delta_{oop}(N-H)$ |
| | | 757 | 37.0 | $\delta_{oop}(C-H)$ |
| 725 | 51.6 | 728 | 28.2 | $\delta_{oop}(C-H)$ |
| 707 | 5.3 | 712 | 9.8 | $\delta_{ip}(ring) + \delta(N-H)$ |
| 662 | 6.6 | 666 | 8.7 | $\delta_{\mathrm{ip}}(\mathrm{CNNC})$ |
| 641 | 17.3 | 642 | 22.7 | $\nu(ring)$ |
| 620 | 15.5 | 619 | 6.6 | $\delta_{ m oop}(m ring)$ |

^{*a*}Estimated at the B3LYP/6-31++G(d,p) level using a scaling factor of 0.98. Vibrational modes with relative intensities less than 5 are omitted, but given in Table S1. ^{*b*}Symbols of v and δ represent stretching and bending modes, and the subscripts of ip and oop represent in-plane and out-of-plane modes, respectively.

wavenumbers are consistent with the corresponding theoretical values for *t*-DBI, although the band calculated at 757 cm⁻¹ may be missed by overlapping with the strongest band at 763 cm⁻¹. Thus, our initial purpose to measure the IR spectrum of a new species DBI was accomplished successfully.

We recognized more interesting phenomenon in the difference spectrum shown in Figure 1, i.e., the decreasing bands were not assigned to the reactant, DAN, but to an unexpected photoproduct ³ANN, which was confirmed by a comparison of the observed spectral pattern with the calculated spectral pattern (Figure 1). The intense decreasing bands observed at 3509/3500, 1604 cm⁻¹ were assigned to the characteristic NH₂ asymmetric stretching and C-NH₂ stretching mode of ³ANN. The both bands observed at 806 and 720 cm⁻ were assigned to the out-of-plane ring bending modes, which were very close to the reported intense bands in this region of 1-naphthylnitrene.¹⁰ The calculated wavenumbers of ³ANN were consistent with the corresponding observed values satisfactorily (Table 2). We also found the backward isomerization from *t*-DBI to ³ANN upon UV irradiation ($\lambda > 350$ nm). The existence of the triplet nitrene ³ANN has been previously reported in the photolysis of 8-amino-1-azidonaphthalene by ESR study¹⁴ but its IR spectrum and reversible photoisomerization have not been known so far.

The nitrene ³ANN showed one more interesting photoisomerization upon visible-light irradiation. A new triplet biradical ³DND was produced from ³ANN by the secondary irradiation ($\lambda > 700$ nm) after the prephotolysis of DAN by 300 nm irradiation, as shown in Figure 2. Three stable

Table 2. Observed and Calculated Wavenumbers (in $\rm cm^{-1})$ of $^3\rm ANN$

| obsd | | calcd ^a | | |
|-----------|------|--------------------|------|-----------------------------------|
| ĩ | abs | ĩ | int | assignment |
| 3509/3500 | 20.7 | 3623 | 18.7 | ν (N-H) |
| 3320 | 11.0 | 3446 | 12.2 | ν (N-H) |
| | | 3141 | 9.1 | ν (C-H) |
| | | 3136 | 6.2 | ν (C-H) |
| 1604 | 100 | 1622 | 100 | ν (C-NH ₂) |
| 1514/1512 | 9.7 | 1520 | 9.2 | $\nu(C-C)$ |
| 1486/1482 | 5.5 | 1489 | 9.3 | $\nu(C-C) + \nu(C-N)$ |
| 1455 | 17.3 | 1457 | 12.3 | $\nu(C-C) + \nu(C-N)$ |
| 1346 | 2.0 | 1352 | 3.2 | ν (C-C) + δ_{ip} (N-H) |
| 1321 | 14.7 | 1331 | 12.6 | ν (C-C) + δ_{ip} (N-H) |
| 1311 | 5.1 | 1320 | 12.3 | $\nu(C-C) + \nu(C-N)$ |
| 1256/1253 | 14.1 | 1256 | 8.2 | ν (C-C) + δ_{ip} (N-H) |
| 1206 | 4.3 | 1207 | 7.5 | ν (C-C) + δ_{ip} (N-H) |
| 1073 | 9.6 | 1072 | 4.5 | $\delta_{ m ip}(m ring)$ |
| 1024 | 2.5 | 1031 | 4.6 | $\delta_{ m ip}(m ring)$ |
| 806 | 44.0 | 791 | 22.8 | $\delta_{ m oop}(m ring)$ |
| 743 | 12.4 | 738 | 1.7 | $\delta_{oop}(C-H)$ |
| 720 | 49.3 | 717 | 21.4 | $\delta_{ m oop}(m ring)$ |

^{*a*}See the captions in Table 1. All the calculation results are given in Table S2.



Figure 2. (a) Dfference spectrum obtained by isomerization from ³ANN to ³DND(2) upon visible-light irradiation ($\lambda > 700$ nm) following the UV preirradiation ($\lambda > 300$ nm). (b) Simulated spectrum composed of the calculated spectral patterns for ³ANN in the downside and ³DND(2) in the upside, obtained at the B3LYP/6-31++G(d,p) level using a scaling factor of 0.98.

conformations of ³DND are possible in association with the relative direction of the two imino groups, as shown in Scheme 1. It is interesting that a simulated spectrum for the most stable conformer ³DND(1), having one hydrogen bond between the hydrogen atom in one imino group and the nitrogen atom in the other imino group, was inconsistent to the observed one (see Figure S3). In contrast to this fact, the second stable conformer ³DND(2) reproduced the difference spectrum satisfactorily, as shown in Figure 2, where the simulated spectrum is composed of the calculated spectral patterns of ³ANN in the downside and ³DND(2) in the upside.

The biradical ³DND(2) has a feature of double interaction between the hydrogen atom of one $^{\circ}N-H$ group and the nitrogen atom in the other $^{\circ}N-H$ group, as shown in Figure 3, where the two imino groups twist from a quasi-planar naphthalene part (see the side view of ³DND(2) in Figures 3



Figure 3. Optimized structures of ³ANN, ³DND(2), and *t*-DBI calculated at the B3LYP/6-31++G(d,p) level. Bond lengths (in Å) of C–N, O–H, and N–N are written; other bond lengths are given in Figure S4.

and S4). The bands observed at 3279, 1143, 823, and 672/669 cm⁻¹ in Figure 2 satisfactorily corresponded to the calculated values of 3401, 1140, 809, and 666 cm⁻¹, respectively, which were assigned to the N–H stretching, the in-plane N–H/C-H bending, the out-of-plane ring bending and the out-of-plane N–H bending modes of ³DND(2), respectively. The band at 3387 cm⁻¹ was assigned to a combination band. A comparison of the observed wavenumbers of ³DND(2) with the corresponding calculated ones is summarized in Table 3. The

Table 3. Observed and Calculated Wavenumbers (in cm⁻¹) of ³DND(2)

| obsd | | calcd ^a | | |
|----------|------|--------------------|------|---------------------------------------|
| ĩ | abs | ĩ | int | assignment |
| 3387 | 1.9 | | | combination |
| 3279 | 1.2 | 3401 | 6.3 | ν (N-H) |
| 3067 | 1.4 | 3139 | 13.3 | ν (C-H) |
| 1550 | 7.0 | 1550 | 6.2 | $\nu(C-C)$ |
| 1519 | 2.5 | 1524 | 10.8 | $\nu(C-C)$ |
| 1385 | 3.3 | 1386 | 19.0 | ν (C–C–N) |
| 1351 | 3.9 | 1354 | 5.4 | $\delta_{ip}(N-H)$ |
| 1342 | 6.4 | 1335 | 10.3 | $\delta_{ip}(N-H) + \delta_{ip}(C-H)$ |
| 1178 | 5.7 | 1161 | 5.5 | $\delta_{ip}(N-H)$ |
| 1143 | 37.6 | 1140 | 34.4 | $\delta_{ip}(N-H) + \delta_{ip}(C-H)$ |
| 1074 | 16.1 | 1073 | 22.0 | $\delta_{ip}(ring)$ |
| 1042 | 17.3 | 1038 | 10.8 | $\delta_{ip}(CCC) + \delta_{ip}(C-H)$ |
| 823 | 100 | 809 | 35.6 | $\delta_{oop}(ring)$ |
| 672/669 | 78.8 | 666 | 100 | $\delta_{oop}(N-H)$ |
| 650 | 11.0 | 646 | 6.6 | $\delta_{ip}(ring)$ |
| <i>a</i> | | | | |

^aSee the captions in Table 1. All the calculation results are given in Table S3.

backward reaction from ³DND(2) to ³ANN upon visible-light irradiation ($\lambda > 500$ nm) was also confirmed. In addition, the photoisomerization from ³DND(2) to *t*-DBI upon 600 nm irradiation was also confirmed (Figure S5). However, the backward reaction from *t*-DBI to ³DND(2) was not induced by any light used in the present study.

It must be explained that no bands of the most stable conformer ³DND(1) and the third stable conformer ³DND(3) were observed upon 700 nm irradiation. One possibility is the conversion from ³DND(1) to ³ANN through the hydrogenatom tunneling, where the transition barrier height, 52.3 kJ mol⁻¹, is too high for the thermal conversion at such lowtemperature condition. On the other hand, ³DND(3) could immediately isomerize to DBI, because the geometrical structures of the both species are similar to each other. However, the energy of ³DBI is predicted to be about 150 kJ mol⁻¹ higher than ³DND(3). Thus, we remove the possibility of the isomerization from ³DND(3) to ³DBI on the triplet potential surface. Another possibility is that ${}^{3}DND(3)$ changes to ${}^{3}DND(1)$, where the barrier height from ${}^{3}DND(3)$ to ${}^{3}DND(1)$ is 27.3 kJ mol⁻¹, and then ${}^{3}DND(1)$ changes to ${}^{3}ANN$ by the tunneling, ${}^{4,15-17}$ resulting in the detection of only the bands due to ${}^{3}DND(2)$, although we have no more experimental evidence on this assumption.

The triplet nitrene ³ANN with a quasi-planar structure is more stable than the singlet one ¹ANN by 92.9 kJ mol⁻¹ (Figure 4). The low triplet-triplet transition energies were



Figure 4. Relative energies of possible photoproducts obtained by the DFT calculations at the B3LYP/6-31++G(d,p) level, where triplet states are drawn by blue lines. Since the relative energies of the lowest triplet states for *t*-DBI, *c*-DBI, 7CK, and azirine are estimated to be 146.78, 210.07, 103.89, and 269.38 kJ mol⁻¹, respectively, they are out of range on this scale.

estimated by the TD-DFT calculation to be 692, 621, and 437 nm, which are consistent with the experimental results on the photoinduced isomerization observed in the present study; ${}^{3}ANN$ changed to ${}^{3}DND(2)$ by 700 nm irradiation and to *t*-DBI by 580 nm irradiation, implying that the former isomerization occurs through the first electronic transition state, while the latter isomerization occurs through the second one.

The low triplet-triplet transition energies of ${}^{3}\text{DND}(2)$ were estimated to be 596, 523, and 467 nm. Our experimental results showed the photoinduced isomerization from ${}^{3}\text{DND}(2)$ to *t*-DBI by 600 nm irradiation, and to ${}^{3}\text{ANN}$ by 500 nm irradiation, respectively. We conclude that the former and the latter correspond to the first (596 nm) and the second (523 nm) calculated transitions. In addition, our DFT calculations summarized in Figure 4 can explain the fact that a seven-membered cyclic ketenimine (7CK) and azirine were undetected in the photolysis of DAN, because they are less stable than *t*-DBI by more than 130 kJ mol⁻¹.

CONCLUSIONS

IR spectra of ³ANN, ³DND(2), and *t*-DBI produced in the photolysis of DAN in an Ar matrix were first measured in the present experiment. By a comparison of the DFT calculations with the observed spectra, the conformations of ³DND(2) and *t*-DBI were determined; the former is the second stable conformer having feature intramolecular interaction in the two imino groups twisted from a quasi-planar naphthalene part; the latter is the more stable conformer having *trans* positions in association with two hydrogen atoms in the NH groups. The prototype isomerization systems from ³ANN to ³DND(2) and to *t*-DBI were found, which was contrast to the well-known reversible isomerization between triplet naphthylnitrenes and the corresponding seven-membered ring compounds.¹⁰ It was

concluded that the photon energies required for the photoreaction processes were explainable in terms of triplet-triplet transition energies estimated by TD-DFT calculations.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b00154.

Comparison of the observed IR spectra with those of the other isomers, their optimized structures, and all wavenumbers theoretically estimated by the B3LYP/6-31++G(d,p), and a complete ref 13 (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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