

A Matrix Isolation, Laser Flash Photolysis, and Computational Study of Adamantene

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Photolysis (350 nm) of 3-noradamantyl diazirine (**5**) in argon at 14 K produces adamantene (**1**) ($\lambda_{\text{max}} = 320$ nm; IR, $\nu = 1478$ cm^{-1}) and protoadamant-3-ene (**8**) ($\lambda_{\text{max}} = 220$ nm; IR, $\nu = 1580$ cm^{-1}). Strained alkenes **1** and **8** can be interconverted photochemically in argon at 14 K. Laser flash photolysis (351 nm) of **5** in benzene solution produces **1**. The decay of **1** is monitored at 325 nm. Absolute rate constants of reaction of **1** with methanol, 1,3-cyclohexadiene, tris(trimethylsilyl)silane, acetic acid, and oxygen are reported.

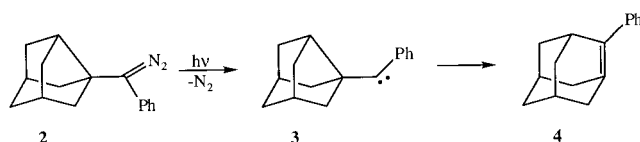
I. Introduction

Bredt was the first to recognize that nature avoids placing double bonds at the bridgehead positions of bicyclic molecules.¹ Adamantene (**1**) is a famous violation of Bredt's rule. Calcula-

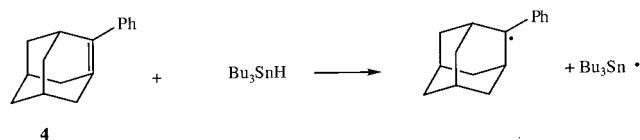


tions indicate that the heat of formation of **1** is 32.36 kcal/mol and that the twist angle between the orbitals making up the π portion of the double bond is 64° .² Adamantene has a large olefinic strain energy of 39.5 kcal/mol,³ and consequently it is a transient species in solution and in the gas phase.⁴ It can be trapped with butadiene to form a Diels–Alder adduct, for example.^{4c,d} In the absence of trapping agents it will dimerize.⁵

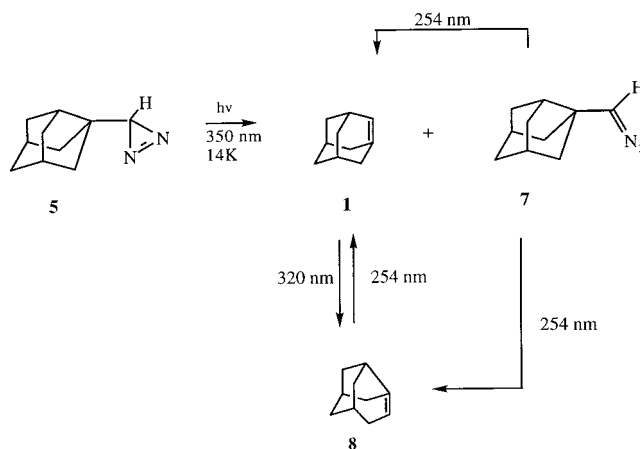
Several workers have generated bridgehead alkenes from the rearrangement of bridgehead carbenes.⁶ Jones⁷ and Michl² and co-workers have generated adamantene from what is formally noradamantylcarbene. Tomioka et al. has generated 1-phenyladamantene (**4**) from a bridgehead diazo precursor (**2**).⁸ The ring expansion of a bridgehead carbene has also been used to prepare tricyclo[2.2.2]-1-octene,⁹ 1-chlorohomoadamantene,¹⁰ homoadamantene,¹¹ and homocubene.^{12,13} The lifetime of **4** in



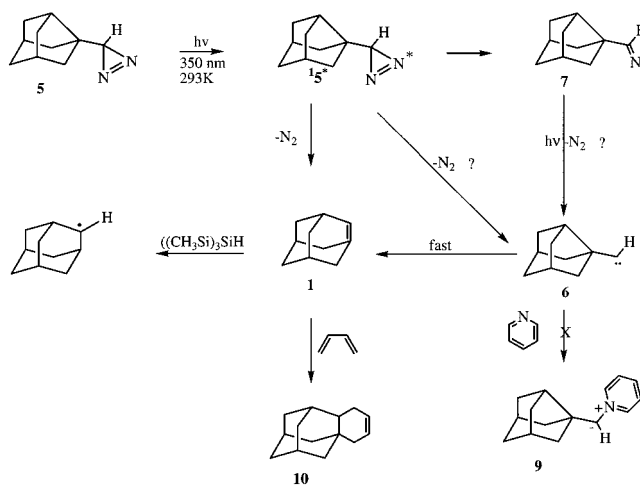
benzene solution was found to be 5.6 ms at ambient temperature. The long lifetime of **4** is not surprising considering that sterically blocked homoadamantenes are remarkably persistent.^{14,15} The strained alkene **4** reacts with methanol with an absolute rate constant of $8.7 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$. The phenyl-substituted bridgehead alkene reacts with oxygen with absolute rate constant $7.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Furthermore, the strained alkene reacts with tri-*n*-butyltin hydride with rate constant $6.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ to form a species with $\lambda_{\text{max}} = 310\text{--}320$ nm, attributed to a benzylic



SCHEME 1



SCHEME 2



radical.⁸ Bridgehead carbene **3** was not trappable with pyridine and was not observed by flash photolysis.

This work stimulated us to synthesize the desphenyldiazirine **5** (Scheme 1). Herein, we are pleased to report the results of this study and absolute rate constants of reaction of **1** with typical quenchers.

II. Experimental Section

General Methods. ¹H NMR spectra were obtained on a Bruker DRX-500 (500 MHz) or Bruker AM-200 MHz spec-

trometer. IR spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer interfaced with a Perkin-Elmer 3700 data station with 2 cm^{-1} resolution. The GC-MS spectrometer was an HP-6890 series GC system with an HP-1 methylsiloxane capillary column ($40.0\text{ m} \times 100\text{ }\mu\text{m} \times 0.20\text{ }\mu\text{m}$). The gas chromatograph was linked to an HP 5973 mass-selective detector.

Benzene, toluene, and cyclohexane were purified by distillation from sodium-benzophenone and stored under an argon atmosphere. 1,3-Cyclohexadiene, 1,3-diphenylbenzofuran, acetic acid, 1,3-butadiene, and tris(trimethylsilyl)silane were purchased from Aldrich Chemical Co. Piperidine and methanol were dried by distillation prior to use.

Laser Flash Photolysis (LFP) Studies. For LFP studies, a stock solution of **5** in benzene was prepared to an optical density of 0.5–1.0 and placed in each cuvette (3 mL per cuvette) with various amounts of trapping agents. For Nd:YAG laser flash studies, suprasil quartz fluorescence free static cells and a special sample holder were used to avoid scattering of the laser beam. The LFP apparatus utilized a Lumonics TE-861-4 excimer laser (351 nm, 60 mJ, 7 ns, KRF excimer) and a Continuum PY62C-10 Nd:YAG laser (355 nm, 30 mJ, 2 ns). Samples used in LFP experiments were deoxygenated by passing a flow of dry argon through the sample for 2 min. The analysis of the data was carried out by the program Igor designed by Wavemetrics. Transient absorption spectra were obtained on an EG&G PARC 1460 optical multichannel analyzer fitted with an EG&G PARC 1304 pulse amplifier, an EG&G PARC 1024 UV detector, and a Jarrell-Ash 1234 grating. The monochromator used was an Oriel 77200. Signals were obtained with a photomultiplier tube detector and were digitized by a Tektonix 5818A A/D transient digitizer. The spectrometer has been described elsewhere in some detail.¹⁶

Matrix Isolation Spectroscopy. The diazirine precursor **5** was placed in a glass U tube which was directly connected to the closed cycle cryogenic system cooled by helium (Air Products). Argon gas blew over the precursor and condensed on the surface of a CsI window. The argon matrix formed was maintained at 14 K during the entire experiment. UV-vis spectra were measured with a Lambda 6 UV-vis spectrophotometer. Ray-O-Net lamps (254 and 350 nm) were used to photolyze the sample, and IR and UV-vis spectra were recorded sequentially in each step of the photolysis cycle.

Density Functional Calculations. Geometries of singlet noradamantylcarbene, adamantene, and protoadamant-3-ene were fully optimized at the B3LYP level using the 6-31G* basis set, and harmonic frequencies were calculated at the same level. All the calculations were carried out with the Gaussian software package.¹⁷

Preparation of 3-Noradamantyldiazirine. 3-Noradamantyl alcohol¹⁸ was prepared by reduction of 3-noradamantanecarboxylic acid (Aldrich) with lithium aluminum hydride (LAH). 3-Noradamantyl alcohol was isolated by column chromatography (33% EtOAc in hexane). The yield was 99%. 3-Noradamantylcarboxaldehyde¹⁹ was prepared from 1 g (6.58 mmol) of 3-noradamantyl alcohol by Swern oxidation.²⁰ The yield of aldehyde¹⁹ was 96%. The desired diazirine was synthesized from the aldehyde. 3-Noradamantylcarboxaldehyde (0.15 g, 1 mmol) was stirred with 2 mL of 1 M lithium bis(trimethylsilyl)amide in 3 mL of THF cooled with an ice bath for 30 min. The mixture was cooled with an acetone-dry ice bath, and then hydroxylamine-O-sulfonic acid (0.12 g, 1 mmol) dissolved in 1 mL of diglyme was added slowly over 30 min. The solution was warmed with an ice bath and stirred for 1 h. *tert*-Butyl

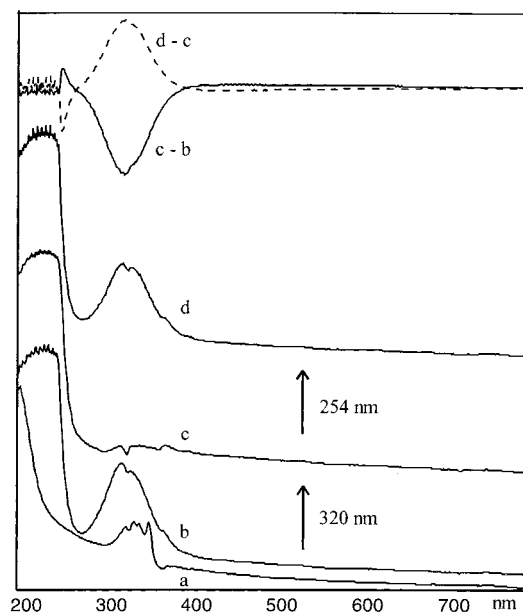


Figure 1. UV-vis spectra obtained upon photolysis of **5** in an argon matrix: (a) before photolysis; (b) after photolysis at 350 nm (33 min); (c) after photolysis at 320 nm (35 min); (d) after photolysis at 254 nm (25 min).

hypochlorite (0.113 mL, 1 mmol) was added to the mixture (cooled in an ice bath), and the resulting mixture was stirred for 1 h. The mixture was extracted with pentane and dried with sodium sulfate. The solvent was evaporated, and then the mixture was chromatographed using only pentane. The yield of 3-noradamantyldiazirine was 67%. ^1H NMR (500 MHz, CDCl_3 , ppm) δ 2.24 (m, 1H), 2.17 (s, 2H), 1.65–1.41 (m, 10H), 0.96 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3 , ppm) δ 47.9, 46.0, 43.8, 41.3, 37.0, 34.9, 26.8; UV-vis λ_{max} 340 nm; IR 1582 cm^{-1} ; MS (EI) m/z (rel intens) 134 ($\text{M}^+ - \text{N}_2$, 1), 119 (17), 105, 91 (100), 77 (67); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}$ ($\text{M}^+ - \text{N}_2$) 134.1096, found 134.1090.

GC-MS Product Study. 1,3-Butadiene was condensed into a solution of **5** in benzene at 273 K. Photolysis (350 nm, Ray-O-Net) produced four adducts as determined by GC-MS. The major adduct was identical (GC retention time, MS fragmentation pattern) with an authentic sample of **10** provided by Professor Jones. An HP-6890 series GC system with an HP-SMS phenylmethylsiloxane capillary column ($300\text{ nm} \times 250\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$) was employed. The GC was linked to an HP 5973 mass-selective detector.

III. Results

Matrix Isolation Spectroscopy. Photolysis (350 nm, 33 min) of 3-noradamantyldiazirine in an argon matrix (curve a, Figure 1) led to the disappearance of the diazirine and to the appearance of new bands at 250 and 320 nm (curve b, Figure 1). The band at 320 nm is assigned to adamantene on the basis of the work of the Michl group.² The band at 250 nm likely contains contributions from protoadamant-3-ene (**8**) and diazo compound **7**² as the IR spectrum of this matrix exhibits an intense band at 2057 cm^{-1} assigned to the latter compound (Scheme 1). Subsequent photolysis of adamantene with 320 nm light (35 min) resulted in the disappearance of the 320 nm band (curve c, Figure 1). The difference spectrum (c) – (b) in the UV-vis region is shown in Figure 1, and that in the IR region is shown in Figure 2.

The (c) – (b) curve shown in Figure 1 and the spectra of curve a in Figure 2 are assigned to **8** (1580 cm^{-1}) on the basis

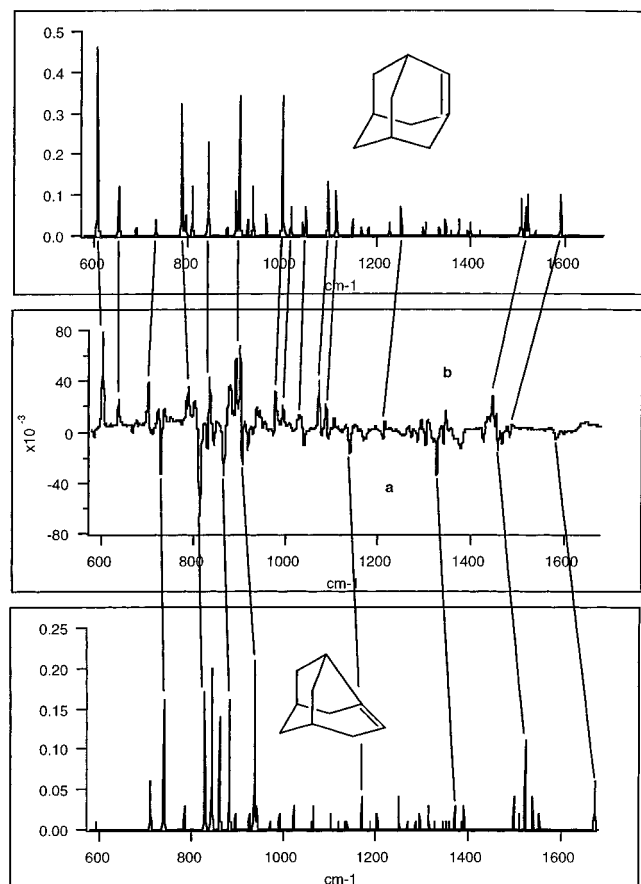


Figure 2. Theoretical and observed IR spectrum of adamantene obtained upon photolysis (350 nm) of 3-noradamantyldiazirine. The spectrum of adamantene (curve b) corresponds to the conditions of (d) – (c) of Figure 1. The IR spectrum of protoadamantene (curve a) corresponds to the conditions of (c) – (b) of Figure 1. The spectrum was calculated at the B3LYP/6-31G* level without scaling.

of a B3LYP/6-31G* calculation (1670 cm^{-1}). Our computational result is in excellent agreement with that of the Michl group (1587 cm^{-1})² (Table 1). Continuous irradiation of the matrix containing protoadamant-3-ene with 254 nm light (25 min) regenerated the 320 nm band (curve d, Figure 1). The difference spectrum (d) – (c) in UV–vis is shown in Figure 1, and the IR spectra are shown in Figure 2 (curve b). The (d) – (c) curve in Figure 1 and curve b in Figure 2 were assigned to **1** (1478 cm^{-1}) on the basis of a B3LYP/6-31G* calculation (1590 cm^{-1}). The reported value of 1481 cm^{-1} for adamantene by Michl² is in good agreement with our experimental and computational work. Full details concerning the results of the calculations can be found in the Supporting Information. This is the first observation of photochemical interconversion between protoadamant-3-ene and adamantene and is summarized in Scheme 1. We posit that photolysis of alkenes **1** and **8** forms bridgehead carbene **6**, which is a transient species in argon at 10 K and which immediately re-forms the olefins. The difference in absorption spectra of **1** and **8** allows one alkene to be pumped to the other isomer. Photochemical transformation of alkenes to carbenes is well-known.²²

The absorption spectra of strained alkenes **1** and **8** was adequately described by INDO/S calculations with single and double excitations.²¹ The geometry optimizations were performed at the B3LYP/6-31G* level with the Gaussian 94 software package. The stationary points were verified by harmonic frequency calculations. The excitation energies of

TABLE 1: Calculated and Experimental Data on the Strained Alkenes Produced on Photolysis of 3-Noradamantyldiazirine

	C=C Stretch frequency		$\pi\pi^*$ Excitation energy	
	exp ^a	calcd ^a	exp ^a	calcd ^a
1	1481 (1478)	1523 ^b (1542) ^c	317 (320)	407 ^d (305) ^e
8	1587 (1580)	1607 ^b (1622) ^c	250 (254)	288 ^d (246) ^e

^a In argon matrix and in the calculations, the top values are those of Michl et al.² and the lower values in parentheses are this work. ^b MNDO value multiplied by 0.915 (a value chosen to optimize agreement for C=C stretch in ethylene and tetramethylethylene). ^c B3LYP/6-31G*, frequencies with a scaling factor of 0.97. ^d INDO/S.²¹ ^e INDO/S with double excitations.²¹

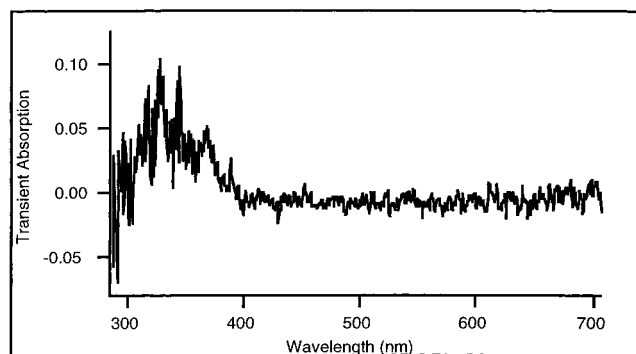


Figure 3. Transient spectrum of **1** produced by LFP of **5** in benzene at ambient temperature. The spectrum was recorded over a window of 200 ns, 300 ns following the laser pulse.

protoadamant-3-ene and adamantene were calculated using the INDO/S method with single and double excitations.²¹

The first excited state of adamantene and protoadamant-3-ene consists of 99% electron promotion from orbital 2 to orbital 3 as shown in the Supporting Information. This is a pure π to π^* excitation. The differences of HOMO to LUMO excitation energies in adamantene and protoadamant-3-ene are 6.8 and 8.2 eV, respectively.

Calculations of noradamantylcarbene and its rearrangement to adamantene and protoadamant-3-ene will be reported elsewhere.²³

LFP Studies. LFP (351 nm, 60 mJ, 17 ns, KrF excimer) of 3-noradamantyldiazirine in benzene at ambient temperature produces the transient absorption spectrum shown in Figure 3. The maximum of the transient spectra is at 325 nm. The carrier of this absorption band is assigned to adamantene on the basis of our own and previously reported matrix experiments.² 2-Phenyladamantene has longer wavelength absorption than does **1**, $\lambda_{\text{max}} = 434\text{ nm}$, due to the extended conjugation of the π system.⁸

Pyridine was added to trap putative carbene intermediate **6**. There was no transient spectrum of an ylide formed in the visible region upon LFP of diazirine **5**. Either the lifetime of 3-noradamantylcarbene (**6**) is too short to permit reaction to form ylide **9** or the yield of carbene **6** produced upon photolysis of **5** is too small to be detected. We suspect²² that some adamantene is formed in a rearrangement of the diazirine excited state in a manner reminiscent of the homocubyl¹³ carbene system. Thus, the yield of carbene and of pyridine ylide **9** in solution is very

TABLE 2: Lifetime and Decay Rate Constant of Adamantene with Representative Quenchers

quencher	$k_Q(1)$, $M^{-1} s^{-1}$	$k_Q(4^8)$, $M^{-1} s^{-1}$	quencher	$k_Q(1)$, $M^{-1} s^{-1}$	$k_Q(4^8)$, $M^{-1} s^{-1}$
methanol	8.4×10^4	8.7×10^1	tri- <i>n</i> -butyltin hydride		6.3×10^4
1,3-cyclohexadiene	1.8×10^5		acetic acid	1.4×10^7	
tris(trimethylsilyl)silane	6.3×10^5		oxygen	5.4×10^7	7.0×10^6

low. Furthermore, it was not possible to trap carbene **6** with piperidine to form an adduct in more than trace quantities.²³ However, photolysis of **5** in the presence of 1,3-butadiene yields a product with the same retention time (gas chromatography) and mass spectral fragmentation pattern as an authentic sample of **10** generously provided by Professor Jones.

1 decays over many microseconds in a second-order process to form a mixture of known dimers. The decay of **1** is accelerated in the presence of a saturating concentration of oxygen by a factor of roughly 3.6. From this it is possible to estimate k_{O_2} as $5.4 \times 10^7 M^{-1} s^{-1}$ (Table 2).

The decay of adamantene is pseudo-first-order in the presence of quenchers (methanol, 1,3-cyclohexadiene, tris(trimethylsilyl)silane, tri-*n*-butyltin hydride, acetic acid) of the strained alkene. The experimental decays are analyzed to yield time constants k_{obs} . Plots of k_{obs} versus the concentration of quencher, Q , are linear (Figure 4). The slopes of these plots represent values of k_Q , the absolute second-order rate constant of reaction of adamantene with quencher (Table 2). Adamantene undergoes reaction with a diene, a hydrogen atom and a proton donor at easily measured rates as expected from its large strain energy and known chemistry.^{2,4,7}

Unsurprisingly, as seen in Table 2, parent adamantene is significantly more reactive than sterically blocked derivative **4**.⁸

IV. Conclusions

3-Noradamantyl diazirine **5** was deposited into an argon matrix at 14 K. Exposure to 350 nm light consumed the diazirine and led to the appearance of the known UV and IR spectra of adamantene. Noradamantylcarbene was not observed in the matrix. Photolysis (320 nm) of matrix-isolated adamantene led to its conversion into protoadamant-3-ene. Photolysis (254 nm) of **8** led to isomerization back to **1**. Strained alkenes **1** and **8** interconvert through the bridgehead carbene. The IR and UV spectra of the strained alkenes are adequately simulated by B3LYP and INDO/S calculations with single and double excitations.

Laser flash photolysis (351 nm) of diazirine **5** in benzene produced the transient spectrum of adamantene ($\lambda_{max} = 325$ nm). The bridgehead carbene was not detected by the pyridine-ylide method. The absolute rate constants of reaction of adamantene were determined with the following quenchers:

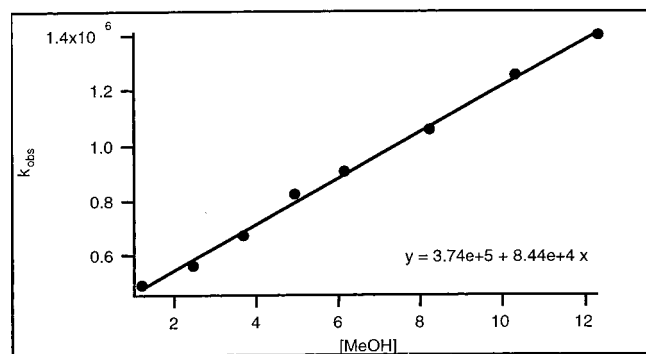


Figure 4. k_{obs} of decay of **1** vs [MeOH] in benzene at ambient temperature.

methanol, $8.4 \times 10^4 M^{-1} s^{-1}$; 1,3-cyclohexadiene, $1.8 \times 10^5 M^{-1} s^{-1}$; acetic acid, $1.4 \times 10^7 M^{-1} s^{-1}$; oxygen, $5.4 \times 10^7 M^{-1} s^{-1}$. Adamantene is considerably more reactive than 2-phenyladamantene.

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Supporting Information Available: Energies and geometries of the stationary points for **1**, **6**, and **8** and configurations and states involved in the electronic transitions of **1** and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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