Reactions of Unsaturated Azides. 11. Direct Observation of 2-Methylene-2*H*-azirine[†,1a]

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Abstract: 2-Methylene-2*H*-azirine (**3a**) was generated by photolysis of azidopropadiene (**2a**) and characterized by low-temperature ^{1}H NMR spectra and IR data of the matrix-isolated substance. Ab initio calculations at the MP2/6-31+G*//MP2/6-31+G* level are reported for **3a** as well as for 3-methyl-2-methylene-2*H*-azirine (**3b**) and are in good agreement with the experimental results. This is shown by comparison of computed versus measured IR spectra of the azatriafulvenes **3a** and **3b**. The contribution of a dipolar canonical structure to the resonance hybrid of **3**, which is the first example of a heterocyclic triafulvene, is discussed.

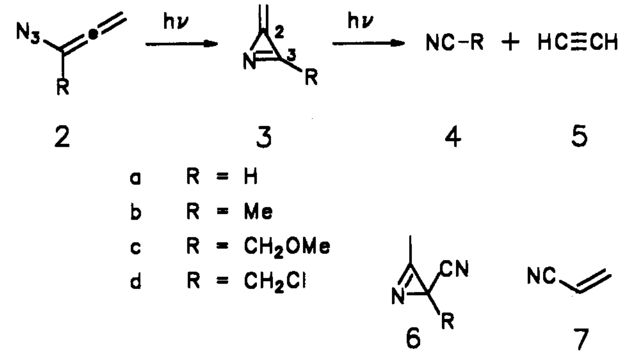
Introduction

As the simplest cross-conjugated cyclic hydrocarbon, methylenecyclopropene (**1a**)[2] has been the object of considerable research effort. Derivatives with an exocyclic heteroatom, like **1b**, have attracted even more attention.[3] However, heterocyclic

1 a X = CH_2
b X = NR, O, S, Se

derivatives are rather rare. For instance, the existence of azirinones[4] was only indicated by plausible hints, and alleged azirinimines[5] as well as 2-methylene-2*H*-azirines[6] proved to be structurally isomeric products.[7,8]

Scheme I



Recently, the isolation of the long-sought 1-azidoallenes **2**[9] was reported; such compounds allow an easy photochemical approach to the substituted 2-methylene-2*H*-azirines **3b–d**.[10] Physical evidence for the parent azatriafulvene **3a** is, however, completely lacking because of the low stability[11] of 3-unsubstituted 2*H*-azirines. Moreover, the synthesis of **3** involves a photochemical consecutive reaction leading to hydrogen cyanide (**4a**) and acetylene (**5**) in the case of **3a**. Since **4a** readily adds to **3** to give **6**, only plausible successive products of **3a**, namely **4a**, **5**, and **6a**, were found in addition to **7** on irradiation of **2a** (Scheme 1).[10] We report here spectroscopic evidence for the parent azatriafulvene **3a**, one of the high-energy,[12] closed-shell C_3H_3N isomers.

Results and Discussion

The azide **2a**,[9] freshly purified by gas chromatography, was mixed with krypton (1:100) in the gas phase and deposited on a metal mirror cooled to 15 K. The matrix was irradiated through a glass filter (λ > 320 nm) using a high-pressure mercury lamp. At several intervals during the photolysis, IR spectra were recorded (Figure 1). At first very strong bands of **2a** (2102, 2168 cm^{-1})

[†] Dedicated to Professor Helmut Quast on the occasion of his 60th birthday.

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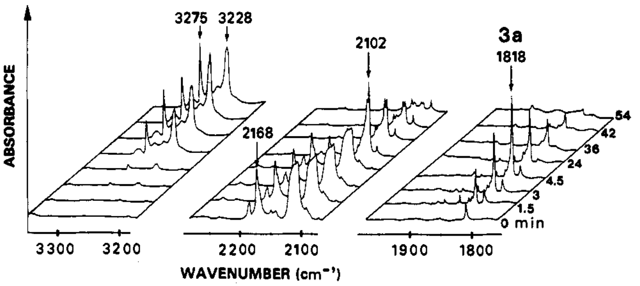

Figure 1. Infrared spectra during photolysis (0–54 min) of **2a** in krypton matrix. The very strong azide band at 2102 cm^{-1} gives rise to saturation effects, which disappear at lower concentrations of **2a**. Below 2000 cm^{-1} the ordinate of the spectra is expanded by a factor of 10.

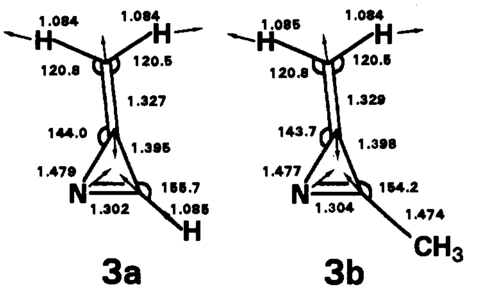

Figure 2. Bond distances (Å) and bond angles (deg) for **3a,b** (C_s) from ab initio calculations. Arrows schematically indicate stretching motions for which IR frequencies of 1818 cm^{-1} for **3a** and 1858 cm^{-1} for **3b** are computed.

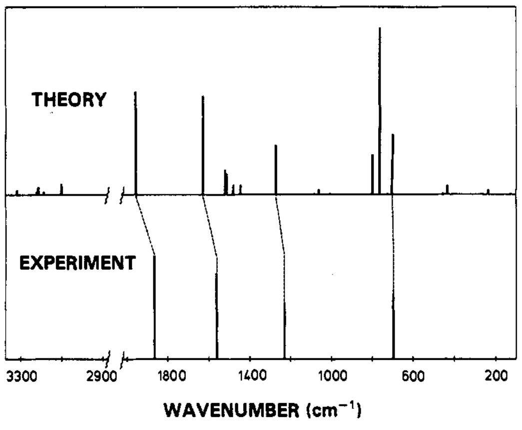

Figure 3. Comparison of the calculated IR spectrum (MP2/6-31+G*//MP2/6-31+G* without scaling factor) with the experimental spectrum of **3b** in krypton matrix. Relative intensities are shown by bar heights. The bands of **2b** and the successive products of **3b** give rise to several superpositions and prevent the experimentally unambiguous detection of further signals resulting from **3b**, particularly in the region of 800–725 cm^{-1}.

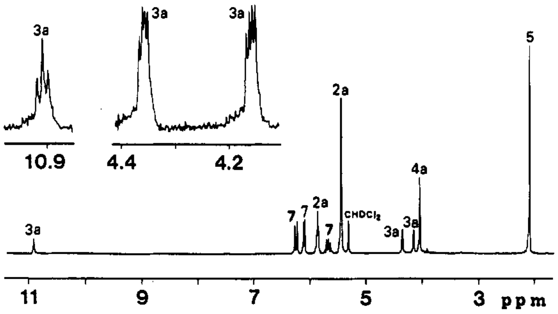

Figure 4. ^{1}H NMR spectrum (400 MHz, CD$_2$Cl$_2$, −94 °C) obtained after irradiation of **2a**. Data for **3a**: δ 10.91 (t, H-3), 4.36 (dd), 4.16 (dd), ^2J = 2.2 Hz, ^4J = $^4J^*$ = 4.0 Hz. Homonuclear couplings are checked by double resonance.

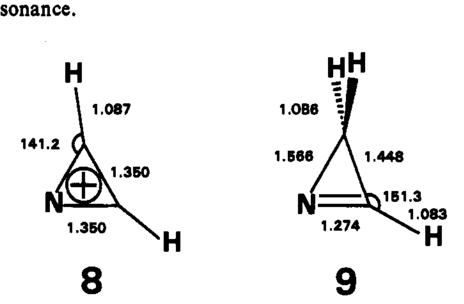

Figure 5. Bond distances (Å) and bond angles (deg) for **8** and **9** from ab initio calculations.

were observed, but an absorption at 1818 cm^{-1} originating from **3a** appeared after a short time of photolysis. Prolonged irradiation led to decreasing absorbance due to **2a** and **3a** while signals attributed to **4a** and **5** (3228, 3275 cm^{-1}) became predominant. Our results demonstrate that photolysis of **2a** produces **3a** and *consecutively* **4a** and **5**.

Structural parameters as well as computed vibrational frequencies for **3a** and **3b** were obtained by ab initio theory using the MP2/6-31+G*//MP2/6-31+G* basis set[13] (Figure 2). Triafulvenes display characteristic IR signals which arise from strong coupling between the two double bonds.[2d,3c] For **3a**, the strongest of these bands was calculated to absorb at 1914 cm^{-1}, or rather at 1818 cm^{-1} when the generally accepted scaling factor of 0.95 was used (Figure 2). According to an analogous computation with the same scaling factor, intense lines at 1858, 1542, 1207, 757, 723, and 666 cm^{-1} were predicted for **3b**. Apart from several superpositions, major IR signals at 1865, 1554, 1228, and 696 cm^{-1} measured for **3b** in krypton matrix are in excellent agreement, and the calculated relative intensities correlate well with the experimental data (Figure 3).

The ^{1}H NMR signals of **3a** were observed besides those of **2a**, **4a**, **5**, and **7** (Figure 4) when a solution of **2a** in CD$_2$Cl$_2$ was irradiated briefly at −94 °C and the spectrum was recorded immediately at the same temperature. In comparison with the data of 2*H*-azirine,[14] the resonance of H-3 of **3a** was shifted significantly to higher frequencies ($\Delta\delta$ = 0.9–1.0 ppm). Even at −94 °C, **3a** was not stable in the presence of **4a**. After very few minutes, the ^{1}H NMR signals of **3a** disappeared and those of the addition product **6a** arose.

Ab initio calculations and experimental results suggest that a dipolar canonical structure contributes to the resonance hybrid of **3**. Since bond lengths in the ring of **3a,b** (Figure 2) differ significantly from results computed for azirinylium ion **8** (Figure 5, see also ref 15), we prefer **3**β to **3**α. Compared to the bond lengths of simple 2*H*-azirines from calculations (Figure 5, see also refs 15b and 16) or X-ray crystal structure analysis,[17] **3a** and **3b** show shorter C(2)—C(3) and C(2)—N bonds as well as substantially longer C(3)=N bonds. Moreover, atomic charges

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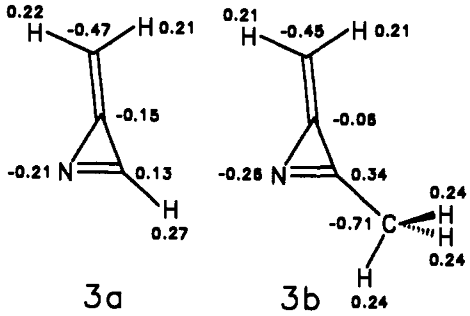
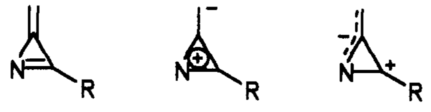


3a 3b



3 3α 3β

Figure 6. Atomic charges obtained using Mulliken population analysis for **3a** and **3b**.

computed from the Mulliken population analysis[18] (Figure 6) as well as ^{1}H and ^{13}C NMR[10] data of **3** and the regioselective 1,4 addition[20] **3** + **4a** → **6** are compatible with a contribution from resonance form **3β**.

Experimental Section

Materials. The azides **2a** and **2b** were purified by gas chromatography (25–50 °C), isolated and handled in traps cooled to –80 °C, and used as soon as possible.[9] *Caution* should be exercised during isolation of azides.

Instrumentation and Sample Preparation. Infrared spectra were recorded with an IFS 113v FT IR spectrometer (Bruker, Karlsruhe). Interferograms were taken by adding 100 scans (ca. 3 min) before applying a Fourier transform. The resolution applied was 1 cm^{-1}. The matrix samples were prepared as thin films on a highly reflecting metal mirror attached to a closed-cycle helium cryostat (Air Products, Model CSW-202).[21]

Gas mixtures of **2a** or **2b** and krypton (molar ratio 1:100) were prepared using standard manometric procedures and deposited at a rate of 90 μmol/min and a deposition temperature of 15 K. Krypton was used as matrix gas since argon led to a comparatively low S/N ratio.

NMR spectra were obtained using a Bruker AMX 400 spectrometer.

Photolyses. Irradiations of **2a** or **2b** were performed by using a high-pressure mercury lamp (TQ 150, Quarzlampengesellschaft Hanau) supplied with glass filters (λ > 320 nm) to minimize the absorption of the photoproducts **3a** or **3b**.

Computational Methods. The geometries of **3a** and **3b** were completely optimized within C_S symmetry using the MP2(FC)/6-31+G*//MP2-(FC)/6-31+G* basis set of the GAUSSIAN 92 series of programs.[13] According to analytical frequency calculations, both structures correspond to minima on the potential energy hyperface (NIMAG = 0). For comparison, geometry optimizations were also performed for the azirinylium ion (**8**) and for 2*H*-azirine (**9**). For the GAUSSIAN archive files, see supplementary material.

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Supplementary Material Available: GAUSSIAN 92 archive entries for optimizations of **3a**, **3b**, the azirinylium ion (**8**), and 2*H*-azirine (**9**) and frequency calculations of **3a** and **3b** (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[18] Although the validity of the Mulliken population analysis has been questioned (refs 2e, 2h, and 19 and references therein) and the quantitative values should be regarded with caution, the method is useful when comparing similar compounds.

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