JOC The Journal of Organic Chemistry
Note
pubs.acs.org/joc

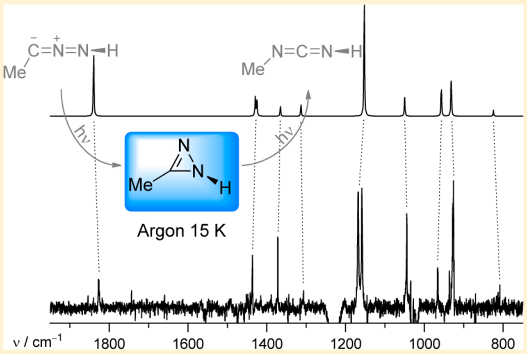
Generation and Characterization of a 4π-Electron Three-Membered Ring 1*H*-Diazirine: An Elusive Intermediate in Nitrile Imine–Carbodiimide Isomerization

Cláudio M. Nunes,[*,†] Cuauhtémoc Araujo-Andrade,[†,‡] Rui Fausto,[†] and Igor Reva[†]

[†]Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[‡]Unidad Académica de Física, Autonomous University of Zacatecas, 98060 Zacatecas, ZAC, Mexico

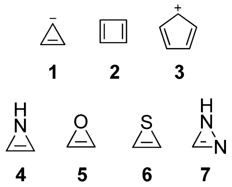
Ⓢ *Supporting Information*

ABSTRACT: The photolysis at 222 nm of 5-methyltetrazole isolated in a cryogenic argon matrix leads to formation of methyl nitrile imine as primary product. Subsequent irradiation at 328 nm induces transformation of the nitrile imine into 4π-electron three-membered-ring 3-methyl-1*H*-diazirine, which photorearranges to give methyl carbodiimide. These products were characterized by IR spectroscopy and theoretical calculations. For the first time, a 1*H*-diazirine was captured as intermediate in the photoisomerization of nitrile imines into carbodiimides.



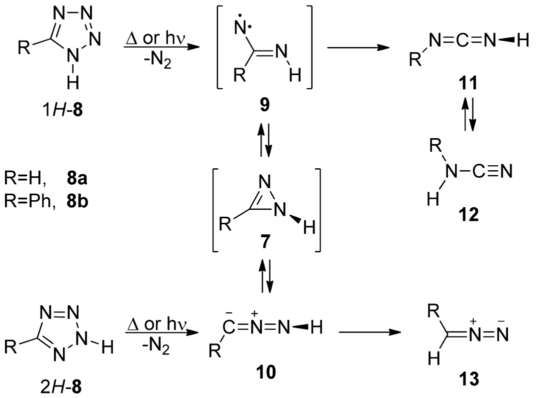
The concept of antiaromaticity, attributed to planar cyclic systems containing 4n π-electrons, was introduced in 1965[1,2] and is now an established paradigm in organic chemistry.[3,4] The term was coined by Breslow, who recognized that molecules containing 4π-electrons, namely derivatives of cyclopropenyl anion (**1**), cyclobutadiene (**2**), and cyclopentadienyl cation (**3**), are destabilized by cyclic conjugation.[1,5,6] Three-membered heterocycles with 4π-electrons are also interesting prototypes of antiaromatic systems. Due to ring strain and assumed antiaromatic electronic destabilization, the generation and characterization of such molecules can be a challenging task. The simplest 4π three-membered rings, 1*H*-azirine (**4**), oxirene (**5**), and thiirene (**6**), have attracted considerable attention,[7−15] and a few derivatives have been prepared under matrix isolation conditions.[16−21] Herein, we report the generation and capture of 3-methyl-1*H*-diazirine, one of the simplest members of the 1*H*-diazirine family (**7**), and its infrared spectroscopic and computational chemistry characterization.

Chart 1. Prototype Antiaromatic Molecules with 4π-Electrons



1*H*-Diazirines **7** have been postulated to play a key role in both the thermolysis and photolysis of tetrazoles **8** (Scheme 1);[22−26] however, they usually escape experimental observation.[27] In a detailed study of the photochemistry of the parent tetrazole **8a**, Maier et al. have identified four CH_2N_2 isomers after photolysis of the matrix-isolated compound: the nitrile imine (**10a**), carbodiimide (**11a**), cyanamide (**12a**), and diazomethane (**13a**) but not the 1*H*-diazirine (**7a**).[25] Recently, Bégué et al. investigated the thermolysis and photolysis of

Scheme 1. Reaction Mechanism for Thermolysis or Photolysis of Tetrazoles 8 Postulated in the Literature[22−26]



Received: December 10, 2013
Published: March 7, 2014

5-phenyltetrazole **8b** and identified similar species.[26] Interestingly, they were able to capture the nitrile imine **10b** in low temperature matrices and demonstrated unequivocally that this species isomerizes to carbodiimide **11b**. However, no intermediates were detected.

In the present work, we studied the photochemistry of matrix-isolated 5-methyltetrazole **8c** (R = Me) using tunable UV-laser irradiation.[28,29] 5-Methyltetrazole **8c** isolated in an argon matrix at 15 K was found predominantly in the 2*H*-tautomeric form, with the 1*H*-tautomer being present only in trace amounts (see the Supporting Information, Figure S1). Irradiation of matrix-isolated **8c** at 222 nm (1 min, ~15 mW) resulted in the elimination of molecular nitrogen and generation of two main products, the nitrile imine **10c** ($\nu(\mathrm{CNN})_{\mathrm{as}}$ = 2138 cm^{-1}) and carbodiimide **11c** ($\nu(\mathrm{NCN})_{\mathrm{as}}$ = 2152 cm^{-1}) (Figure 1 and Figure S2, Supporting Information). These products were clearly assigned by comparison of the experimental and the B3LYP/cc-pVTZ calculated IR spectra (for more details, see Figure S3, and Tables S1 and S2, Supporting Information). The identification is also supported by previous results obtained in the photolysis of matrix-isolated tetrazoles **8a** and **8b**.[25,26]

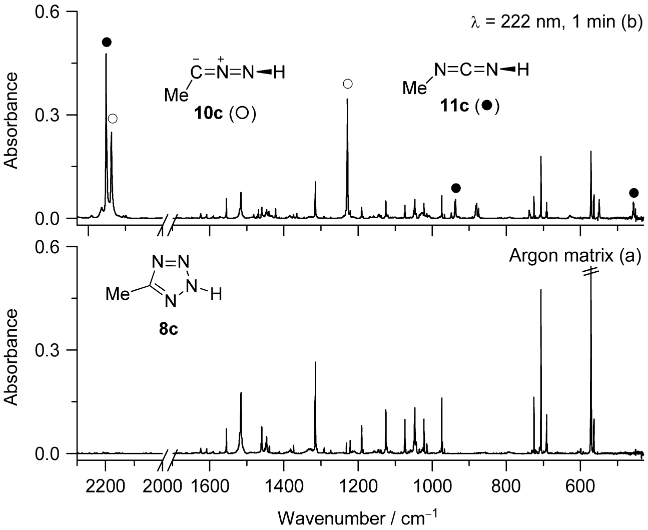


Figure 1. (a) Experimental IR spectrum of 5-methyltetrazole (**8c**) isolated in an argon matrix at 15 K. (b) Experimental IR spectrum after 1 min of UV irradiation at 222 nm (15 mW) of matrix-isolated **8c**. The main products (with most intense IR bands labeled) are nitrile imine **10c** (○) and carbodiimide **11c** (●). More assignment details are given in Figure S3 and Tables S1 and S2 (Supporting Information).

The analysis of photolysis kinetics of **8c** at 222 nm led to several relevant conclusions: (i) nitrile imine **10c** is essentially the only species formed in the first 5 s of irradiation, (ii) carbodiimide **11c** is formed subsequently, and (iii) the amounts of both products increase when irradiation proceeds but the **11c**:**10c** ratio increases (Figure S2, Supporting Information). These results suggest that carbodiimide **11c** is formed via nitrile imine **10c**, in agreement with the observed photorearrangement of **10b** to **11b** reported by Bégué et al.[26,30]

After the irradiation of **8c** at 222 nm and the generation of **10c** in a maximum amount, we performed irradiations using UV light of longer wavelengths, i.e., under conditions where **8c** does not react but its photoproducts can be transformed. By starting at 375 nm and gradually decreasing the wavelength of the tunable UV-laser source, it was observed that irradiations at around 330 nm affect the bands of photoproducts of **8c**. Irradiations at ~328 nm[31] for 100 s resulted in selective photoreaction of nitrile imine **10c** and formation of an unknown intermediate with a distinctive absorption band at 1826 cm^{-1}, whose IR spectrum in the fingerprint region is shown in Figure 2a. From the comparison between the experimental and the B3LYP/cc-pVTZ calculated IR spectra, we unambiguously identify this species as the elusive 1*H*-diazirine **7c** (Figure 2, Table 1).

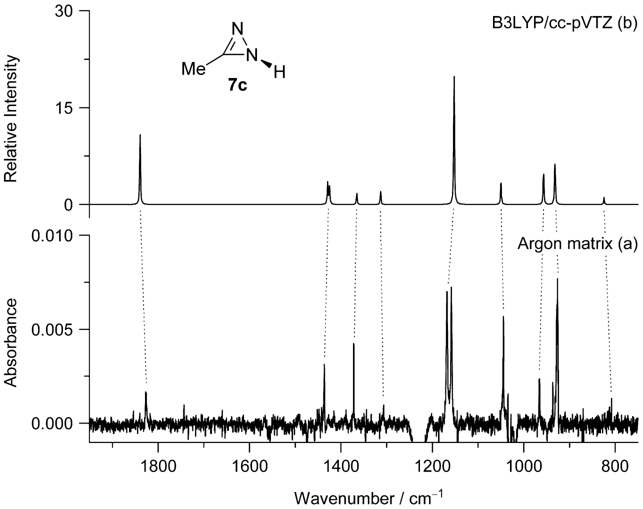


Figure 2. (a) Experimental difference IR spectrum resulting from photochemistry of **10c** at ~328 nm (100 s, ~30 mW) in an argon matrix at 15 K. The negative bands (truncated) correspond to nitrile imine **10c**, and positive bands are due to the product. (b) IR spectrum of 1*H*-diazirine **7c** simulated at the B3LYP/cc-pVTZ level.

The absorption bands expected for **7c** in the fingerprint region above 550 cm^{-1} are all clearly observed and assigned (Table 1). Particularly characteristic is the band at 1826 cm^{-1}, assigned to the $\nu(\mathrm{C{=}N})$ stretching mode calculated at 1839 cm^{-1}. The most intense band, which appears split into two components at 1168 and 1158 cm^{-1}, correlates well with the calculated band at 1152 cm^{-1}, with significant contributions from the C–N stretching, NH bending and methyl group rocking coordinates. The bands in the 1440–1360 cm^{-1} region are assigned to the three methyl bending modes. The band at 1306 cm^{-1} correlates well with the band estimated at 1313 cm^{-1}, which corresponds mainly to the $\delta(\mathrm{CNH})$ bending mode. All other bands, observed at 1044, 966, 928/926, and 808 cm^{-1}, also show an excellent agreement with the calculated data; they are all assigned to modes exhibiting a complex mixture of coordinates (see Table 1).

After detecting 1*H*-diazirine **7c** and upon continued irradiation at 328 nm, we observed the formation of carbodiimide **11c** in a large amount, concomitantly with the consumption of nitrile imine **10c** (see Figure S3, Supporting Information). The photoreaction kinetics of **10c** induced by laser irradiation at 328 nm was studied in detail in a dedicated experiment. The data clearly showed that 1*H*-diazirine **7c** is a photochemical intermediate in the nitrile imine **10c** → carbodiimide **11c** isomerization (Figure 3). This conclusion is based on the following observations: (i) during the initial instants of UV-irradiation (up to 2 min) practically all reacting nitrile imine **10c** is transformed into 1*H*-diazirine **7c**. At this stage, carbodiimide **11c** is almost not produced; (ii) at 15 min

Table 1. Observed Bands in the Fingerprint Range of the Experimental IR Spectrum (Argon Matrix at 15 K) and Calculated (B3LYP/cc-pVTZ) Vibrational Frequencies ($\tilde{\nu}$, cm^{-1}), Absolute Intensities (A, km mol^{-1}), and Vibrational Assignment (PED, %) of 1*H*-Diazirine **7c**.[a]

Ar matrix[b]		calcd[c]		assignment[d]
$\tilde{\nu}$	I	$\tilde{\nu}$	A	PED
1826	m	1839	33.9	ν(N=C)[80], ν(C−C)[12]
1438/1436	m	1429	11.5	$\delta_{as}(CH_3)$[83]
1438/1436	m	1425	10.0	$\delta_{as}'(CH_3)$[84]
1371	m	1365	5.5	$\delta_s(CH_3)$[87]
1306	w	1313	6.6	+δ(CNH)[71], +ν(C−N)[11]
1168/1158	s	1152	63.2	+ν(C−N)[25], −δ(CNH)[23], δ_{as}(CCH)[22]
1044	m	1049	12.7	+δ_s(CCH)[41], γ(C−C)[30], −τ(NH)[14]
966	m	956	16.9	δ_{as}(CCH)[32], δ_s(CCH)[21], τ(NH)[17], ν(C−N)[13]
928/926	s	931	23.4	+τ(NH)[49], +δ_s(CCH)[17], δ_{as}(CCH)[16], ν(C−C)[11]
808	w	824	3.5	ν(C−C)[52], ν(C−N)[24], ν(N−N)[17]

[a] 1*H*-Diazirine **7c** was generated in an argon matrix by irradiation of nitrile imine **10c** at ~328 nm.[31] [b] Experimental intensities are presented in qualitative terms: s = strong, m = medium and w = weak. [c] The calculated B3LYP/cc-pVTZ frequencies were scaled by a factor of 0.969, obtained from the least-squares linear fit (see Figure S4, Supporting Information). [d] Abbreviations: ν, bond stretching; δ, bending; γ, out-of-plane; τ, torsion; s, symmetric; as, antisymmetric. The combinations (+,+) and (+,−) denote in-phase and in-opposite-phase couplings between coordinates of different types. See Table S3 (Supporting Information) for definition of internal coordinates. PED values lower than 10% are omitted.

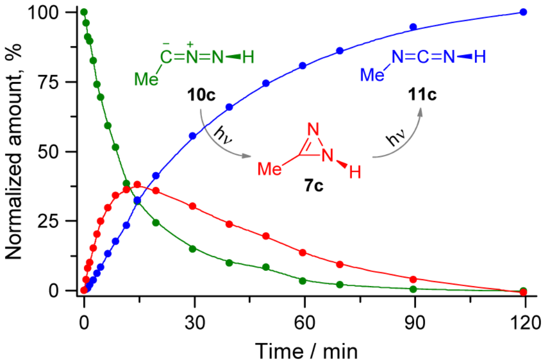
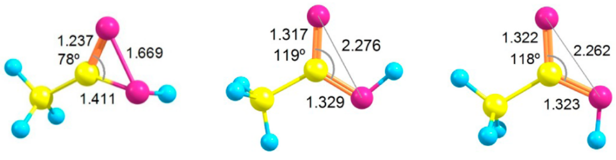


Figure 3. Kinetics of photoisomerization of matrix-isolated nitrile imine **10c** (green) to carbodiimide **11c** (blue) via 1*H*-diazirine **7c** (red) in the course of UV irradiation at 328 nm. See the Experimental Section for details. The inserted scheme summarizes the mechanism of the observed transformation.

of UV-irradiation the amount of 1*H*-diazirine **7c** reaches its maximum and gradually decreases afterward (see also Figure S5, Supporting Information); (iii) after 60 min of irradiation, when virtually all nitrile imine **10c** is consumed, carbodiimide **11c** is still produced which occurs at the expense of the remaining amount of 1*H*-diazirine **7c**.

Finally, it should be mentioned that the geometry of **7c** optimized at the B3LYP/cc-pVTZ level (Figure 4 and Table S4, Supporting Information) indicates an unusually long N−N bond (1.67 Å) and a large N=C−N angle (78°), features that suggest some structural relation with an imidoylnitrene-type structure (for instance, see triplet ^{3}**9c** in Figure 4 and Table S4, Supporting Information). Most of known nitrenes have a triplet ground state followed by an open-shell singlet.[32,33] In contrast, acyl- and aroylnitrenes (RC(O)N; R = H, alkyl and aryl) appear to have a closed-shell singlet ground-state.[34−37] However, it is not clear whether these singlet ground-state species should be designated as nitrenes or cyclic oxazirenes. In the case of **7c**, this structure appears to be better described as a 1*H*-diazirine (3-membered ring) rather than as an imidoylnitrene (acyclic type structure).[38] Note that no other structure similar to **7c** was found on the singlet state surface, but the geometry optimization of **7c** on the triplet manifold converges to structure ^{3}**9c** (N···N distance = 2.28 Å and N=C−N angle = 119°, see Figure 4 and Table S4, Supporting Information) which is clearly an imidoylnitrene species.[39]



7c *syn*-^{3}**9c** *anti*-^{3}**9c**

Figure 4. Structures and selected geometric parameters of 1*H*-diazirine **7c** and triplet imidoylnitrene ^{3}**9c** optimized at the B3LYP/cc-pVTZ level. Bond lengths in angstroms, angles in degrees. Atom color codes: blue, H; yellow, C; magenta, N. For more details, see Table S4 (Supporting Information).

For the eight $H_4C_2N_2$ isomers shown in Figure 5, the B3LYP/cc-pVTZ- and CBS-QB3-calculated energies indicate that 1*H*-diazirine **7c** is the most energetic species in singlet state; ~4 and ~32 kJ mol^{-1} below the nitrene triplet state ^{3}**9c**, respectively.[40] The high energetic character of **7c** (204 kJ mol^{-1} above the carbodiimide **11c** for B3LYP and 191 kJ mol^{-1} above the cyanamide **12c** for CBS-QB3) is conceivably due to both ring strain and antiaromatic destabilization. Our findings for $H_4C_2N_2$ isomers are similar to the trends found in calculations for H_2CN_2 isomers, which can be formed in the photolysis and thermolysis of the parent tetrazole **8a**.[25,41] Thus, it is not entirely surprising that the 1*H*-diazirine **7a** have escaped from experimental observation and only the six most stable isomers on the H_2CN_2 potential energy surface (carbodiimide **11a**, cyanamide **12a**, diazo derivative **13a**, 3*H*-diazirine **14a**, nitrile imine **10a**, and isocyanamide **15a**) had been identified.[25,41]

In summary, we have generated and captured the 4π-electron three-membered-ring 3-methyl-1*H*-diazirine **7c** under low-temperature matrix isolation conditions and characterized it by IR spectroscopy and theoretical calculations. We have proved for the first time, based on the studies performed on this prototype molecule, that (i) elusive 1*H*-diazirines can be generated photochemically from nitrile imines and undergo subsequent photoconversion into carbodiimides and (ii)

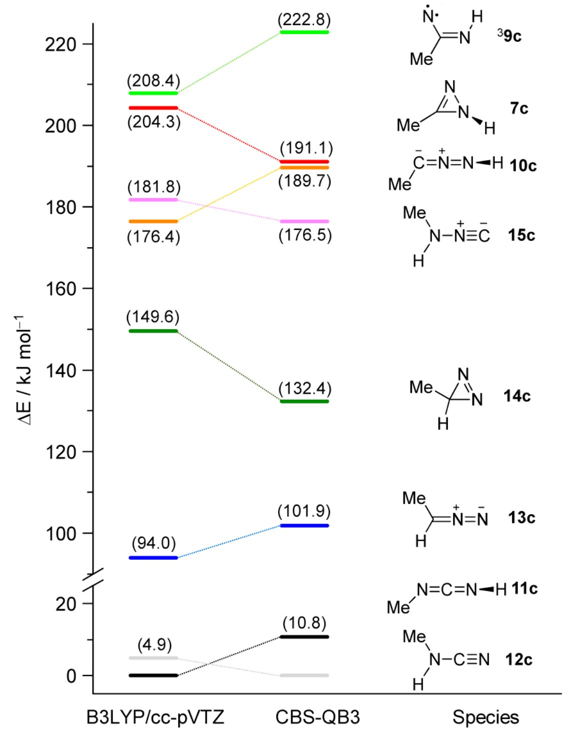


Figure 5. Energies of eight $H_4C_2N_2$ isomers calculated at the B3LYP/cc-pVTZ level and CBS-QB3 level (with the ZPE correction included). The energies in parentheses (in kJ mol^{-1}) are relative to the most stable isomer. The species at right are shown according to the stability order from the CBS-QB3 calculation.

1*H*-diazirines exhibit a close structural relation to imidoylnitrenes and are highly energetic intermediates that play a key role in the general tetrazole chemistry.

■ EXPERIMENTAL SECTION

Sample. A commercial sample of 5-methyltetrazole **8c** (TCI Europe, 98%) was used.

Matrix Isolation FTIR Spectroscopy. Matrices were prepared by codeposition of vapors of **8c**, sublimated at room temperature, with a large excess of argon (N60, Air Liquide) onto a CsI window cooled to 15 K. The temperature was measured directly at the sample holder window by a silicon diode sensor connected to a digital controller providing stabilization accuracy of 0.1 K. A closed-cycle helium refrigeration system was used in the experiments. The IR spectra were recorded with 0.5 cm^{-1} resolution using a FTIR spectrometer, equipped with a mercury cadmium telluride (MCT-B) detector and a Ge/KBr beam splitter. Modifications of the sample compartment of the spectrometer were done to accommodate the cryostat head and allow purging of the instrument by a stream of dry air.

UV-Laser Irradiation Experiments. The matrices were irradiated through an outer quartz window of the cryostat, using a narrow band (fwhm ~0.2 cm^{-1}) frequency-doubled signal beam provided by an optical parametric oscillator (OPO) pumped with a pulsed Nd:YAG laser (repetition rate = 10 Hz, pulse energy ~1−3 mJ, duration = 10 ns). We used UV light at 222 nm to induce the initial photochemistry of **8c** because it is the lowest wavenumber available in our OPO system and it is the closest to the absorption maximum of **8c** (**8c**, UV/vis (H_2O) λ_{max} ~206 nm).

Kinetic Measurements. The starting point (0 min) of the kinetics shown in Figure 3 corresponds to the final stage of the UV irradiation at λ = 222 nm of matrix-isolated 5-methyltetrazole **8c**. The 222 nm irradiation was carried out with the purpose to generate the maximum amount of matrix-isolated nitrile imine **10c**. Simultaneously, some amount of **11c** was produced and traces of **7c** were observed (fragments of infrared spectra shown in Figure S5, Supporting Information). When the irradiation at λ = 328 nm started, the relative amounts of **10c**, **7c**, and **11c** were considered to be 100%, 0%, and 0%, respectively. After 120 min of this irradiation, **10c** was completely consumed (the absolute amount of **10c** equal to 0%), and the produced amount of **11c** was set to 100%. At 15 min, the combined amount of **10c** and **11c** was ~62% and reached the minimum. The remaining amount was parametrized to 38% of **7c**, with a scaling factor K_{max} as the maximum amount of **7c** produced at this stage. At other stages of irradiation, all normalized amounts of **7c** were scaled by K_{max}. All the amounts of species shown in Figure 3 were projected from the experimentally observed integrated infrared intensities of absorptions with maxima at 2138 (**10c**), 1168/1158 (**7c**), and 2152 cm^{-1} (**11c**).

Theoretical Calculations. All calculations were carried out using GAUSSIAN 09.[42] Geometry optimizations followed by harmonic frequency calculations were performed at the B3LYP/cc-pVTZ and CBS-QB3 levels. To correct for the vibrational anharmonicity, basis set truncation, and the neglected part of electron correlation, the B3LYP/cc-pVTZ calculated frequencies were scaled by a factor of 0.969 obtained by least-squares linear fit of the experimental versus calculated frequencies of **7c** (Figure S4, Supporting Information). The calculated frequencies, together with intensities, were then used to simulate the spectra by convoluting each peak with a Lorentzian function with a full width at half-maximum (fwhm) of 2 cm^{-1}. The peak intensities of the simulated spectra (in arbitrary units of "relative intensity") are several times less than the calculated intensities (in km mol^{-1}).

Normal coordinate analyses were carried out in the internal coordinates space, as described by Schachtschneider and Mortimer,[43] using the optimized geometries and harmonic force constants resulting from the B3LYP/cc-pVTZ calculations. The internal coordinates used in these analyses were defined according to the recommendations of Pulay et al.[44]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing experimental and calculated IR spectrum of 5-methyltetrazole **8c**; kinetic progress of photochemistry of **8c** at 222 nm; photorearrangement of nitrile imine **10c** to carbodiimide **11c** after irradiation at 328 nm; least-squares linear fit of the experimental versus calculated frequencies of **7c**; selected regions of spectra showing the kinetics of phototransformations of **10c** to **11c** via **7c** induced by irradiations at 328 nm. Tables of experimental and calculated IR spectra of **10c** and **11c**; definition of internal coordinates for **7c**; calculated geometric parameters for **7c** and **³9c**; Cartesian coordinates, electronic energies and calculated infrared spectra for structures **7c**−**15c** optimized at the B3LYP/cc-pVTZ and CCSD/cc-pVTZ levels. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cmnunes@qui.uc.pt.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

These studies were partially funded by the Portuguese "Fundação para a Ciência e a Tecnologia" (FCT), FEDER, and projects PTDC/QUI-QUI/111879/2009, PTDC/QUI-QUI/118078/2010, and FCOMP-01-0124-FEDER-021082, cofunded by QREN-COMPETE-UE. The Coimbra Chemistry Centre is supported by the FCT through the project PEst-OE/QUI/UI0313/2014. C.M.N. acknowledges the FCT for the Postdoctoral Grant No. SFRH/BPD/86021/2012. C.A.-A.

acknowledges CONACyT, Mexico, Project No. 153066 and the sabbatical grant 203398. We thank Prof. Teresa M. V. D. Pinho e Melo and Prof. Hugh D. Burrows for the helpful discussions.

■ REFERENCES

(1) Breslow, R. *Chem. Eng. News* **1965**, *43*, 90.

(2) Dewar, M. J. S. In *Advances in Chemical Physics*; Wiley: New York, 1965; p 65.

(3) Carey, F. A.; Sundberg, F. J. *Advanced Organic Chemistry. Part A: Structure and Mechanism*, 5th ed.; Springer: New York, 2007.

(4) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 6th ed.; John Wiley & Sons: New York, 2007.

(5) Breslow, R. *Pure Appl. Chem.* **1971**, *26*, 111.

(6) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393.

(7) Hess, B. A., Jr.; Schaad, L. J.; Ewig, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 2507.

(8) Torres, M.; Lown, E. M.; Gunning, H. E.; Strausz, O. P. *Pure Appl. Chem.* **1980**, *52*, 1623.

(9) Alcamí, M.; de Paz, J. L. G.; Yáñez, M. *J. Comput. Chem.* **1989**, *10*, 468.

(10) Zavoruev, S. M.; Rakauskas, R.-I. I. *Theor. Exp. Chem.* **1990**, *25*, 481.

(11) Byun, Y.; Saebo, S.; Pittman, C. P., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689.

(12) Kroeker, R.; Bachrach, S.; Kass, S. *J. Org. Chem.* **1991**, *56*, 4062.

(13) Alcamí, M.; Mó, O.; Yáñez, M. *J. Am. Chem. Soc.* **1993**, *115*, 11074.

(14) Vacek, G.; Galbraith, J.; Yamaguchi, Y.; Schaefer, H. F., III; Nobes, R. H.; Scott, A. P.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 8660.

(15) Malar, E. J. P. *Tetrahedron* **1996**, *52*, 4709.

(16) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1977**, *99*, 4842.

(17) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486.

(18) Regitz, M.; Arnold, B.; Danion, D.; Schubert, H.; Fusser, G. *Bull. Soc. Chim. Belg.* **1981**, *90*, 615.

(19) Torres, M.; Bourdelande, J. *J. Am. Chem. Soc.* **1983**, *105*, 1698.

(20) Bachmann, C.; N'Guessan, T. Y.; Debû, F.; Monnier, M.; Pourcin, J.; Aycard, J.-P.; Bodot, H. *J. Am. Chem. Soc.* **1990**, *112*, 7488.

(21) Maier, G.; Endres, J. *Chem.—Eur. J.* **1999**, *5*, 1590.

(22) Fischer, S.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 502.

(23) Guimon, C.; Gracian, F.; Begtrup, M.; Pfister-Guillouzo, G. *Chem. Phys.* **1989**, *138*, 157.

(24) Bertrand, G.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 527.

(25) Maier, G.; Eckwert, J.; Bothur, A.; Reisenauer, H. P.; Schmidt, C. *Liebigs Ann. Chem.* **1996**, 1041.

(26) Bégué, D.; Qiao, G. G.; Wentrup, C. *J. Am. Chem. Soc.* **2012**, *134*, 5339.

(27) To the best of our knowledge, observation of 1*H*-diazirines **7** has only been reported in a few works limited to the matrix isolation studies concerning the photochemistry of disubstituted tetrazoles conducted in our research group (a−d), and to an NMR reaction monitored study, at −50 °C, where a complex 1*H*-diazirine derivative with heavy phosphoranyl and phosphino substituents was characterized as an intermediate (e). See: (a) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Phys. Chem. A* **2005**, *109*, 7967. (b) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Mol. Struct.* **2006**, *786*, 128. (c) Gómez-Zavaglia, A.; Reva, I. D.; Frija, L.; Cristiano, M. L.; Fausto, R. *J. Photochem. Photobiol. A* **2006**, *180*, 175. (d) Frija, L. M. T.; Reva, I. D.; Gómez-Zavaglia, A.; Cristiano, M. L. S.; Fausto, R. *J. Phys. Chem. A.* **2007**, *111*, 2879. (e) Dubau-Assibat, N.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1996**, *118*, 5216.

(28) Nunes, C. M.; Reva, I.; Pinho e Melo, T. M. V. D.; Fausto, R. *J. Org. Chem.* **2012**, *77*, 8723.

(29) Nunes, C. M.; Reva, I.; Fausto, R. *J. Org. Chem.* **2013**, *78*, 10657.

(30) Toubro et al. also reported the photoisomerization of diphenylnitrilimine to diphenylcarbodiimide in a low-temperature poly(vinyl chloride) matrix. See: Toubro, N. H.; Holm, A. *J. Am. Chem. Soc.* **1980**, *102*, 2093.

(31) Hereafter, the series of irradiations at 330 nm (30 s), 325 nm (20 s), and 328 (60 s) nm we designate as "irradiation at ∼328 nm for 100 s".

(32) Platz, M. S.; Nitrenes. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M. J., Eds.; Jonh Wiley and Sons: New York, 2004; Chapter 11, p 501.

(33) Nunes, C. M.; Reva, I.; Pinho e Melo, T. M. V. D.; Fausto, R.; Šolomek, T.; Bally, T. *J. Am. Chem. Soc.* **2011**, *133*, 18911 and references cited therein.

(34) Gritsan, N. P.; Pritchina, E. A. *Mendeleev Commun.* **2001**, *11*, 94.

(35) Pritchina, E. A.; Gritsan, N. P.; Maltsev, A.; Bally, T.; Autrey, T.; Liu, Y.; Wang, Y.; Toscano, J. P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1010.

(36) Liu, J.; Mandel, S.; Hadad, C. M.; Platz, M. S. *J. Org. Chem.* **2004**, *69*, 8583.

(37) Zeng, X.; Beckers, H.; Willner, H.; Grote, D.; Sander, W. *Chem.—Eur. J.* **2011**, *17*, 3977.

(38) The topological analysis using the Laplacian of the electron charge density reported for the parent 1*H*-diazirine indicates a bonding interaction between the two nitrogen atoms (see ref 15). Additionally, it is known from the gas-phase structure determination that some molecules can have long N−N bonds. For example, the dinitrogen tetroxide (N_2O_4), $r(N-N) = 1.782$ Å, and dinitrogen trioxide (N_2O_3), $r(N-N) = 1.864$ Å (see the list of experimental bond lengths for bond type rNN at the National Institute of Standards and Technology (NIST) website; http://cccbdb.nist.gov/expbondlengths1a.asp?descript=rNN, accessed on March 15, 2014).

(39) Note that the calculated vibrational spectrum of ^{3}**9c** is not compatible with the experimental spectrum of the matrix-isolated photoproduct shown in Figure 2a.

(40) It is not surprising that CBS-QB3 estimates the imidoylnitrene triplet state ^{3}**9c** ∼32 kJ mol^{-1} above 1*H*-diazirine **7c** and B3LYP/cc-pVTZ produces a difference of only ∼4 kJ mol^{-1}. Indeed, it is known that B3LYP calculations usually predict the triplet nitrene to be too stable relative to CBS-QB3 (by approximately ∼33−38 kJ mol^{-1}), which predicts better the energy of these species (see ref 36). In an attempt to obtain a more accurate estimation of the relative energies of the $H_4C_2N_2$ isomers, we also carried out in the present work geometry optimizations and vibrational calculations at the CCSD/cc-pVTZ level (see the Supporting Information). However, we should mention that for some of these isomers (including diazirine **7c** and nitrile imine **10c**) the wave function was found to exhibit an RHF → UHF instability. For the B3LYP and CBS-QB3 calculations no instabilities were found. The B3LYP and CBS-QB3 calculations presented here should be interpreted from a semiquantitative perspective and with some caution. A comprehensive theoretical characterization of the $H_4C_2N_2$ potential energy surface requires multireference calculations, which are beyond the scope of this work.

(41) Ogilvie, J. F.; Wang, F. Theoretical and Experimental Models of Molecules Illustrated with Quantum-Chemical Calculations of Electronic Structure of H_2CN_2 Isomers. In *Models, Mysteries and Magic of Molecules*; Boeyens, J. C. A., Ogilvie, J. F., Eds.; Springer: New York, 2008; Chapter 16, p 341.

(42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.;

Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.2*; Gaussian, Inc., Wallingford, CT, 2009.

(43) Schachtschneider, J. H.; Mortimer, F. S. *Vibrational Analysis of Polyatomic Molecules. VI. FORTRAN IV Programs for Solving the Vibrational Secular Equation and for the Least-Squares Refinement of Force Constants*; Project No. 31450: Structural Interpretation of Spectra; Shell Development Co.: Emeryville, CA, 1969.

(44) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.

■ NOTE ADDED IN PROOF

Recently a paper was published on the photochemical transformations of 5-methyltetrazole isolated in argon matrices by M. Pagacz-Kostrzewa, J. Krupa, M. Wierzejewska, J. *Photochem. Photobiol. A* **2014**, *277*, 37.