THE JOURNAL OF PHYSICAL CHEMISTRY A

Article

Cite This: *J. Phys. Chem. A* 2018, 122, 6852−6855

pubs.acs.org/JPCA

Direct Observation of an Alkylidenecarbene by Ultrafast Transient Absorption Spectroscopy

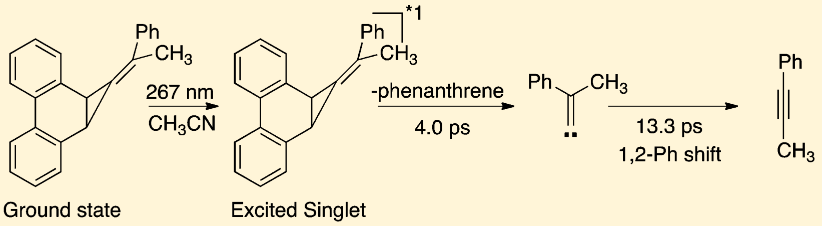
Lili Du,[†] Xin Lan,[†] David Lee Phillips,*[,†] William H. Coldren,[‡] Christopher M. Hadad,*[,‡] Xi Yang,[§] and Dasan M. Thamattoor*[,§]

[†]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

[‡]Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

[§]Department of Chemistry, Colby College, Waterville, Maine 04901, United States

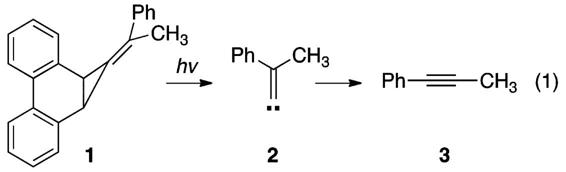
Supporting Information



ABSTRACT: Singlet α-methylbenzylidenecarbene has been detected and characterized for the first time by femtosecond transient absorption (fs-TA) spectroscopy. The carbene was generated by photolysis of the hydrocarbon precursor, 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]-phenanthrene, in acetonitrile. The photolysis initially forms the singlet excited state of the precursor which then extrudes α-methylbenzylidenecarbene in 4.0 ps. The decay of α-methylbenzylidenecarbene, which was previously shown to rearrange into phenylpropyne by a 1,2-phenyl shift, occurred over 13.3 ps. Computed spectra at the TD-B3LYP/6-311+G** level of theory are consistent with the experimental observations. CASSCF(10,10)/6-311+G** calculations, using one of the carbene conformers as a model, indicated that the reference wave function is dominated by a closed-shell description.

■ INTRODUCTION

We recently reported that the phenanthrene-based methylenecyclopropane, 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]-phenanthrene (**1**), produced singlet α-methylbenzylidenecarbene (**2**) upon photolysis in solution (eq 1).[1] The carbene then undergoes a Fritsch−Buttenberg−Wiechell (FBW)-type rearrangement[2−4] to produce the corresponding alkyne **3**. Furthermore, using ^{13}C-labeled precursors that produced **2** with the label at the benzylic carbon, we demonstrated that the rearrangement of **2**-^{13}C occurs exclusively by a 1,2-phenyl shift rather than a methyl shift.[1] These experimental observations were found to be consistent with the results of theoretical calculations.[1]



Remarkably, although time-resolved laser flash photolysis (LFP) has played a critical role in studying various types of carbenes,[5−12] there appear to be no reports attesting to the use of this method for the investigation of alkylidenecarbenes. Perhaps this conspicuous void in the literature may be attributed to the lack of photochemical precursors suitable for such studies. Herein we report a photochemical study of precursor **1** using femtosecond transient absorption (fs-TA) spectroscopy to directly detect and characterize the alkylidenecarbene **2**. To the best of our knowledge, this work is the first direct spectroscopic observation of an alkylidenecarbene in solution.

■ METHODS

The synthesis of precursor **1** was carried out by a procedure that we have previously reported. The description of the experimental set up to perform fs-TA measurement has also been provided in prior publications.[13,14] Calculations were performed, using the Gaussian '16 suite of programs,[15] for comparison of theoretical predictions with the experimental results.

■ RESULTS AND DISCUSSION

Photolysis of **1** was investigated by fs-TA in MeCN solution by irradiation at 267 nm (Figure 1). The initial spectrum at 1 ps

Received: June 26, 2018
Revised: August 1, 2018
Published: August 1, 2018

DOI: 10.1021/acs.jpca.8b06118
J. Phys. Chem. A 2018, 122, 6852−6855

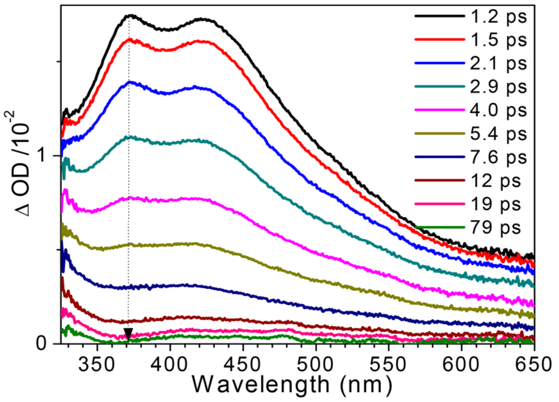


Figure 1. Fs-TA UV−vis spectra of precursor **1** obtained after 267 nm excitation in MeCN.

shows broad bands at 372 and 421 nm. Both of these bands decay rapidly from 1.2 to 12 ps, while the 325 nm tail feature from a higher energy band increases in relative intensity to these two bands. However, due to the limitation of our instrumentation, we were not able to observe the spectra below 325 nm. The relative intensity of the 325 nm tail reaches a maximum at 12 ps, as both bands at 372 and 421 nm subside to the baseline. Subsequently, the tail at 325 nm decays over the next 60 ps.

At the TD-B3LYP/6-311+G** level of theory,[16−20] the ground state of phenanthrene precursor **1** is calculated to have a strong absorption around 280 nm in CH_3CN and the longest wavelength absorption occurs at about 300 nm (see Supporting Information). The optimized (relaxed) S_1 excited state of the photoprecursor (**1**) is calculated in the gas phase to have a λ_{max} of 357 nm and a much weaker (about 20 times) absorption at 437 nm (by comparison of the computed oscillator strengths). The solvated (CH_3CN), relaxed S_1 state has strong absorptions predicted at 340 and 370 nm and a slightly weaker absorption at 449 nm (see Supporting Information). These absorbances are consistent with the longer wavelength peaks that are observed in the transient absorption spectrum that decay over time.

Our previous DFT calculations (B3LYP/6-311+G**) indicated that singlet carbene (^{1}**2**) has two nearly degenerate conformations, one with the methyl group coplanar to the phenyl ring (^{1}**2-pl**) and the other, a nonplanar version, with the methyl group twisted out of plane (^{1}**2-npl**).[1] To evaluate if ^{1}**2** possessed a multireference wave function, CASSCF(10,10)/6-311+G** calculations[21] were employed using the planar carbene (^{1}**2-pl**) geometry as a model. The active space included ten electrons and ten orbitals, three π and three π^* orbitals from the benzene ring, one π and one π^* orbital from the vinyl group, and one sp hybrid type orbital and one unhybridized p-type orbital on the terminus of the vinyl group. The final one-electron density matrix reveals that 9.6 electrons are localized to the five occupied orbitals and only 0.4 electrons are localized in the LUMO+1 and LUMO+2 orbitals (see Supporting Information). The geometry for the planar carbene species was optimized and verified to be a local minimum by vibrational frequency analysis. These CASSCF results are consistent with the previous DFT results. As the CASSCF reference wave function is dominated by a closed-shell description, geometry optimizations, frequency analyses, and vertical excitations for the two conformers of ^{1}**2** were performed at the B3LYP/6-311+G** level of theory both in the gas phase and with an implicit solvation model (SMD, acetonitrile).[22] Local minima were characterized by the absence of imaginary vibrational frequencies. These calculations reveal that the twisted geometry is lower in energy than the planar form by 0.5 kcal/mol (ΔG) with implicit solvation. Additionally, the dihedral angle of the twisted geometry goes from 69° in the gas phase to 85° in acetonitrile, as shown in Figure 2. It is noteworthy that the twisted geometry looks particularly well oriented for phenyl migration. The angles containing carbons two, three, and the divalent carbon are 109° in the gas phase and 86° in acetonitrile (Figure 2).

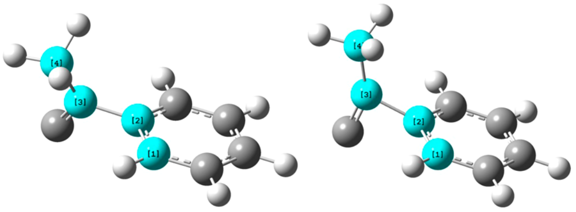


Figure 2. Optimized geometries of carbene ^{1}**2-npl** in the gas phase (left) and acetonitrile (right).

Calculations were performed at the TD-B3LYP/6-311+G** level of theory on both conformers of the carbene in the gas phase as well as with implicit solvation (CH_3CN). In either phase, the maximum absorbance wavelengths for both of these conformers are predicted to be below 300 nm (see Supporting Information). In solution, the twisted carbene (^{1}**2-npl**) has a computed λ_{max} at 206 nm, and two separate, though only slightly weaker, absorbances at 249 and 288 nm as well as a very weak absorbance at 328 nm. In acetonitrile, the planar carbene (^{1}**2-pl**) has a predicted λ_{max} located at 222 and 265 nm. The calculated UV−vis spectra of both forms of ^{1}**2** (planar and nonplanar) are displayed in Figure 3.

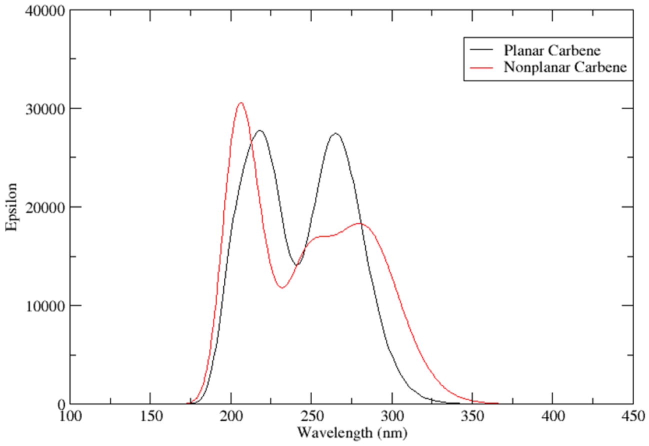


Figure 3. Computed UV−vis spectrum (TD-B3LYP/6-311+G**//B3LYP/6-311+G**) of planar (black) and nonplanar (red) carbene ^{1}**2** in acetonitrile.

Although, the positioning of the maximal absorbance wavelength cannot be observed in the experimental spectrum, the tail observed at 325 nm is tentatively assigned to the carbene intermediate. Even though the energies of the planar and nonplanar forms of ^{1}**2** are nearly degenerate, the calculated UV−vis spectrum of the nonplanar form of the carbene (^{1}**2-npl**) is in better agreement with the experimental results at 12 ps in Figure 4. Therefore, the decreasing intensities of the bands at 372 and 421 nm, which could be attributed to the singlet excited state of the precursor **1**,[23] spontaneously give rise to a new longer-lived intermediate, namely the singlet carbene ^{1}**2**.

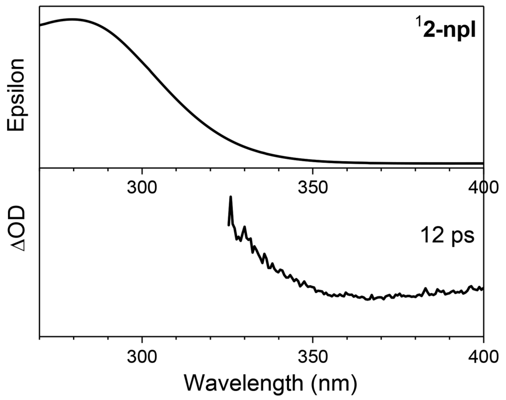


Figure 4. Computed (top) UV−vis spectrum (TD-B3LYP/6-311+G**) and the observed (bottom) fs-TA spectrum at 12 ps in MeCN solution of nonplanar carbene ^{1}**2-npl**.

The temporal dependences of the transient absorption intensity of the initial species at 372 and 325 nm are displayed in Figures 5 and 6, respectively. The kinetics at 372 nm could be fit by a single exponential function as shown in Figure 5, and the time constant for decay of the singlet excited state of **1** as well as the generation of the ^{1}**2** is around 4.0 ps.

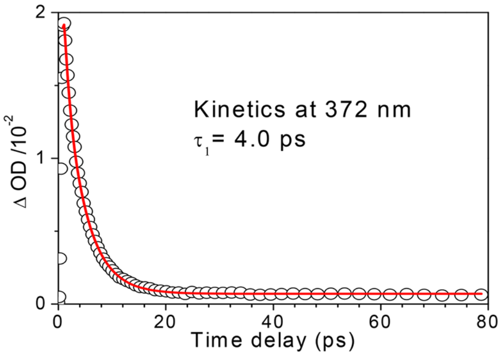


Figure 5. Kinetics at 372 nm of precursor **1** after excitation by 267 nm are shown. The solid red line indicates a fitting of the data using a single exponential function.

Furthermore, as can be seen from Figure 6, ^{1}**2** decays over a period of 13.3 ps, which can be taken as the upper limit for the rate of the 1,2-phenyl shift, the primary pathway converting ^{1}**2** into 1- phenylpropyne **3**. The alkyne product does have a calculated λ_{max} at 262 nm (see Supporting Information), which is relatively close to calculated absorbances of the carbene species, but as the 325 tail grows in and then decays to baseline, it is unlikely to be related to the alkyne product. It is likely the decay of the 325 nm peak would correspond to a peak that rises around 260 nm with a similar time constant of 13.3 ps, but this portion of the UV−vis spectrum was not observable.

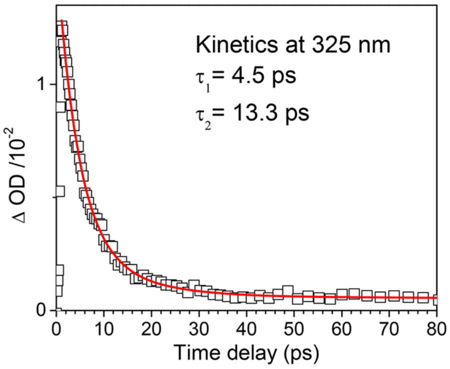


Figure 6. Kinetics at 325 nm of precursor **1** after excitation by 267 nm. The solid red line indicates a fitting of the data using a single exponential function.

■ CONCLUSIONS

In summary, we have used fs-TA UV−vis spectroscopy to observe the generation of alkylidenecarbene ^{1}**2** from the corresponding phenanthrene-based precursor, **1**, in 4.0 ps. The conversion of ^{1}**2** into the alkyne **3** via the known 1,2-phenyl shift was found to occur over 13.3 ps.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b06118.

> fs-TA UV-vis spectra, computational procedures, Cartesian coordinates and vibrational frequencies for all species described in this study, CASSCF final one-electron density matrix for planar carbene, tables of vertical excitations, and IR spectrra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*D. L. Phillips. E-mail: phillips@hku.hk.
*C. M. Hadad. E-mail: hadad.1@osu.edu.
*D. M. Thamattoor. E-mail: dmthamat@colby.edu.

ORCID

Xin Lan: 0000-0002-6745-2154
David Lee Phillips: 0000-0002-8606-8780
Dasan M. Thamattoor: 0000-0002-6619-4392

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.M.T. thanks the National Science Foundation (CHE-1665278) for support of this work and for support by grants from the Research Grants Council of Hong Kong (HKU 17307916) to D.L.P. The Grants Committee Areas of Excellence Scheme (AoE/P-03/08) and the Special Equipment Grant (SEG HKU/07) and a University Development Fund grant for the "New Ultrafast Spectroscopy Experiments for Shared Facilities" from the University of Hong Kong are also gratefully acknowledged. C.M.H. acknowledges generous computational resources from the Ohio Supercomputer Center.

REFERENCES

(1) Yang, X.; Languet, K.; Thamattoor, D. M. An Experimental and Computational Investigation of (α-Methylbenzylidene)carbene. *J. Org. Chem.* **2016**, *81*, 8194−8198.

(2) Fritsch, P. On the Preparation of Diphenylacetaldehyde and a New Synthesis of Tolene Derivatives. *Justus Liebigs Ann. Chem.* **1894**, *279*, 319−323.

(3) Buttenberg, W. P. Condensation of the Dichloroacetal with Phenol and Toluene. *Justus Liebigs Ann. Chem.* **1894**, *279*, 324−337.

(4) Wiechell, H. Condensation of Dichloroacetate with Anisole and Phenetol. *Justus Liebigs Ann. Chem.* **1894**, *279*, 337−344.

(5) Moss, R. A.; Wang, L.; Hoijemberg, P. A.; Krogh-Jespersen, K. Visualizing Carbene Equilibria. *Photochem. Photobiol.* **2014**, *90*, 287−293.

(6) Moss, R. A. Solvation and Complexation of Carbenes - a Perspective. *J. Phys. Org. Chem.* **2011**, *24*, 866−875.

(7) Moss, R. A. Ionic and Radical Fragmentations of Alkoxyhalocarbenes - a Perspective. *J. Phys. Org. Chem.* **2009**, *22*, 265−273.

(8) Moss, R. A.; Tian, J.; Chu, G.; Sauers, R. R.; Krogh-Jespersen, K. New Mechanisms Centered on Reactive Intermediates: Examples from Diazirine and Carbene Chemistry. *Pure Appl. Chem.* **2007**, *79*, 993−1001.

(9) Bonneau, R.; Liu, M. T. H. 1,2-Hydrogen Migration in Carbenes: Laser-Flash Photolysis and Beyond. In *Adv. Carbene Chem.*; Brinker, U. H., Ed.; JAI Press: Stamford, CT, 1998; Vol. *2*, pp 1−28.

(10) Toscano, J. P. Laser Flash Photolysis Studies of Carbonyl Carbenes. In *Adv. Carbene Chem.*; Brinker, U. H., Ed.; JAI Press: Stamford, CT, 1998; Vol. *2*, pp 215−244.

(11) Jackson, J. E.; Platz, M. S. Laser Flash Photolysis Studies of Ylide-forming Reactions of Carbenes. In *Adv. Carbene Chem.*; Brinker, U. H., Ed.; Jai Press: Stamford, CT, 1994; Vol. *1*, pp 89−160.

(12) *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; 372 pp.

(13) Du, L.; Qiu, Y.; Lan, X.; Zhu, R.; Phillips, D. L.; Li, M.-D.; Dutton, A. S.; Winter, A. H. Direct Detection of the Open-Shell Singlet Phenyloxenium Ion: An Atom-Centered Diradical Reacts as an Electrophile. *J. Am. Chem. Soc.* **2017**, *139*, 15054−15059.

(14) Asad, N.; Deodato, D.; Lan, X.; Widegren, M. B.; Phillips, D. L.; Du, L.; Dore, T. M. Photochemical Activation of Tertiary Amines for Applications in Studying Cell Physiology. *J. Am. Chem. Soc.* **2017**, *139*, 12591−12600.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. *Gaussian 16*, Revision A.03; Gaussian, Inc.: Wallingford, CT, 2016. See Supporting Information for complete citation.

(16) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648−52.

(17) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−9.

(18) McLean, A. D.; Chandler, G. S. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, Z = 11−18. *J. Chem. Phys.* **1980**, *72*, 5639−48.

(19) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III. The 3-21+ G Basis Set for First-Row Elements, Lithium to Fluorine. *J. Comput. Chem.* **1983**, *4*, 294−301.

(20) Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-Consistent Molecular Orbital Methods. 25. Supplementary Functions for Gaussian Basis Sets. *J. Chem. Phys.* **1984**, *80*, 3265−9.

(21) Hegarty, D.; Robb, M. A. Application of Unitary Group Methods for Configuration Interaction Calculations. *Mol. Phys.* **1979**, *38*, 1795−812.

(22) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−96.

(23) Wang, J.; Burdzinski, G.; Kubicki, J.; Platz, M. S. Ultrafast UV-Vis and IR Studies of p-Biphenylyl Acetyl and Carbomethoxy Carbenes. *J. Am. Chem. Soc.* **2008**, *130*, 11195−11209.