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UNIVERSITÄT
GIESSEN

*Institute of Organic Chemistry*
*Justus-Liebig University*

# *Reactive Organophosphorus Species and Beyond*

Artur Mardyukov

October 9, 2020

# Known Triplet/Singlet Phosphinidenes

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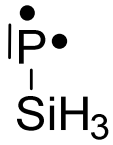
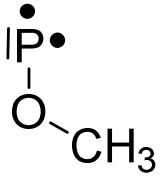
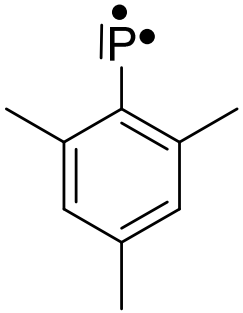
## Triplet Phosphinidenes



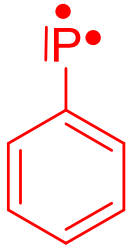
Glaathaar and Maier, Angew. Chem., **2004.** 43, 1294.



Zeng et al., JACS, **2018.** 140, 13604..



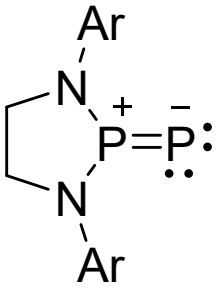
Gaspar, JACS, **1992**, 8526. Lammertsma and Bucher, Angew. Chem. Int. Ed, **2005.** 117, 3353. Akimov et al., Angew. Chem. Int. Ed, **2017**, 56, 7944.



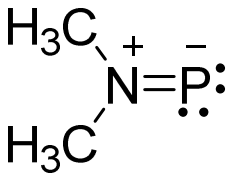
**1**

Mardyukov et al., JACS, **2017.** 139, 5019..

## Singlet Phosphinidenes



Bertrand et al., *Chem* **2016**, 1, 147..

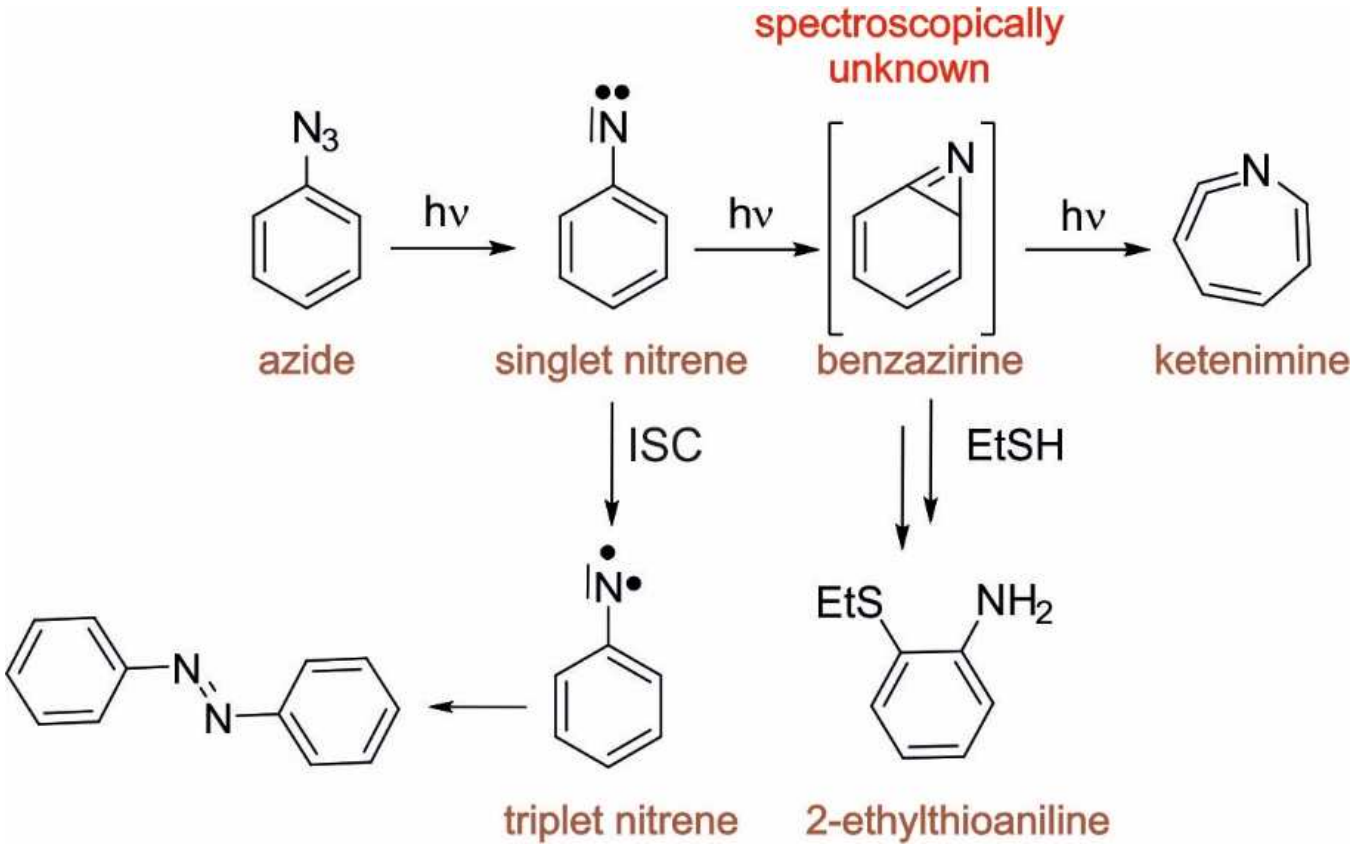


Cummins et al., JACS, **2017.** 139, 10822.

*Mathey, F. In Multiple Bonds and Low Coordination in Phosphorus Chemistry: Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany 1990; p 34.*

# Summary of Experimental Findings - Phenylnitrene






*Borden et al., Acc. Chem. Res, 2000, 33, 765.*

# Calculated bond lengths in the triplet and in the lowest and the first-excited singlet states of PhN and PhP

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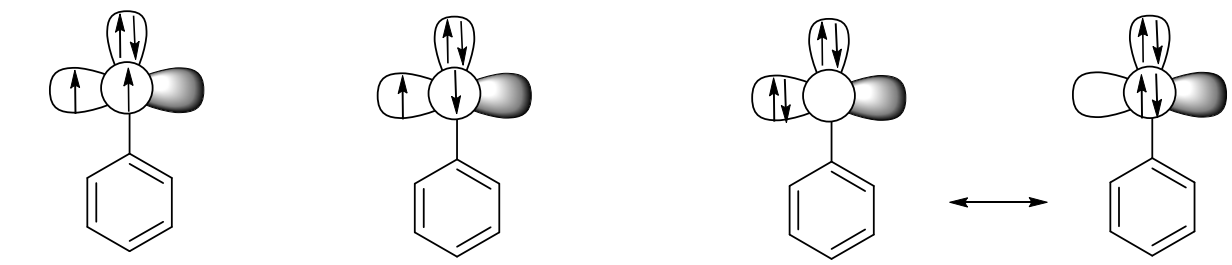

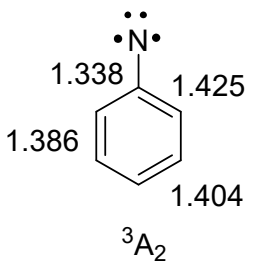


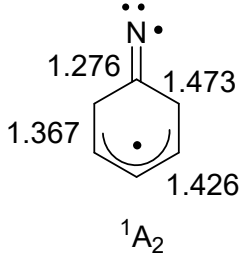


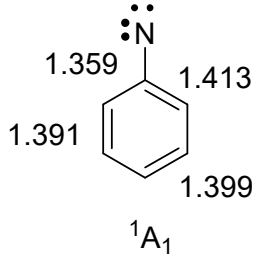


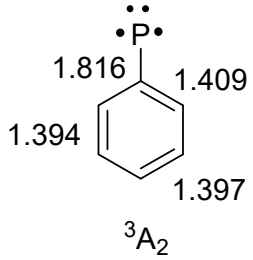


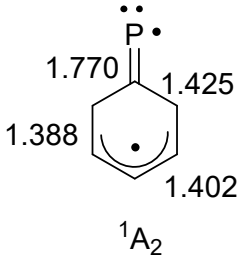


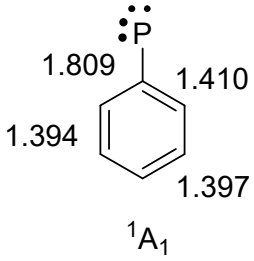


CASSCF/6-31G*

*(a) Borden et al., JACS,* 2002,124, 11669. (b) *Borden et al., Acc. Chem. Res, 2000, 33, 765.*

# Difference between singlet phenylphosphinidene and singlet phenylnitrene in reactivity toward ring expansion

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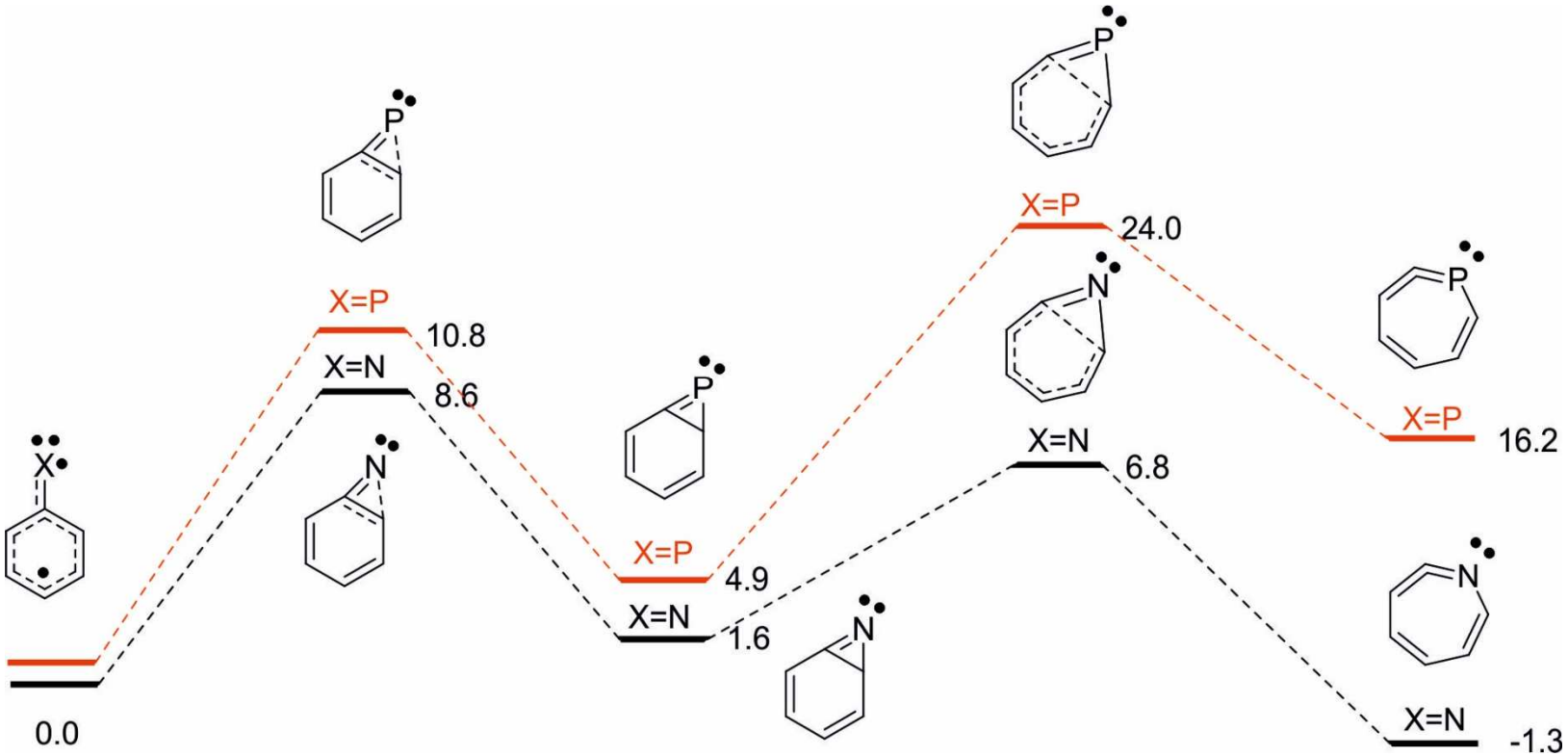
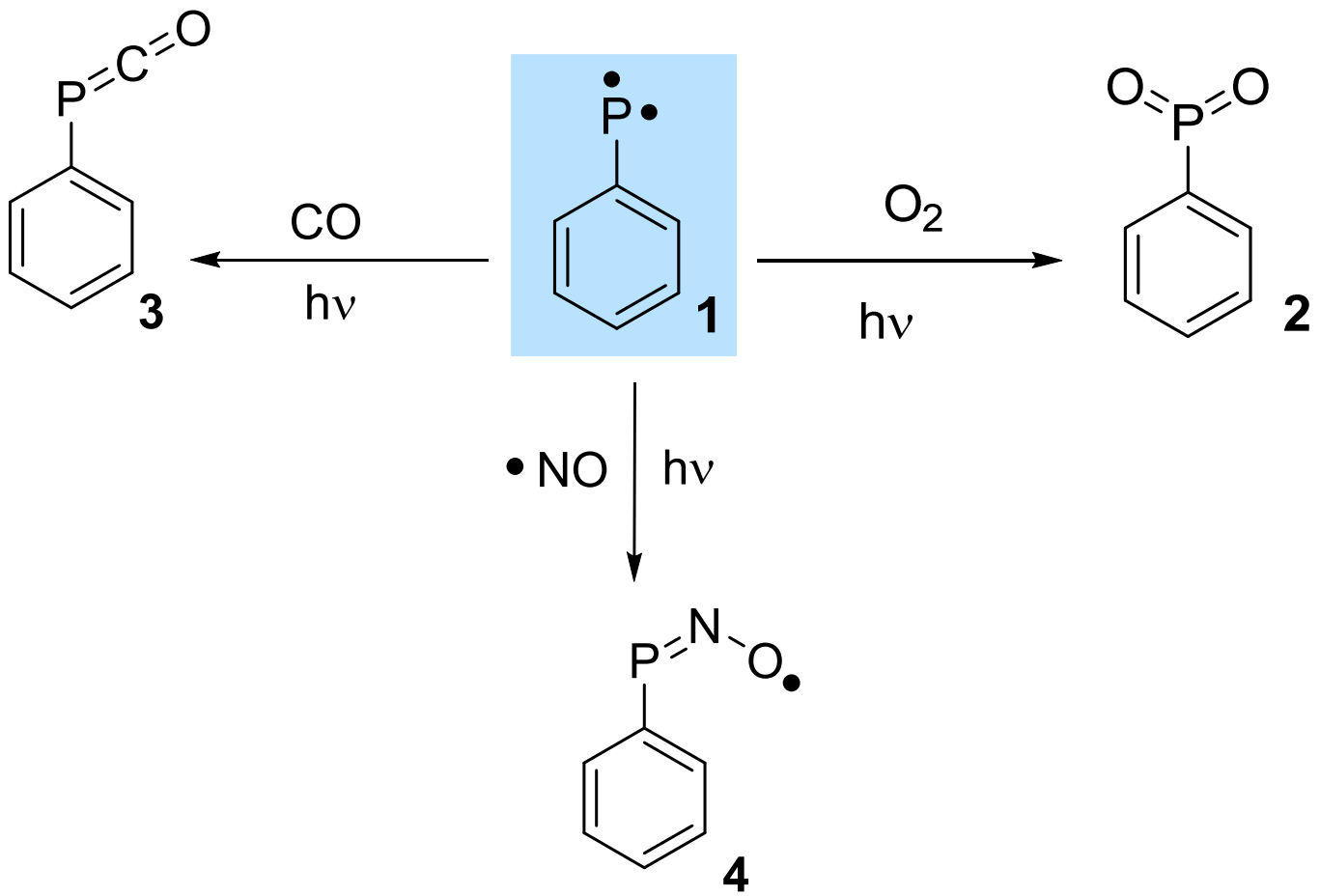



Zero-point inclusive, (8/8)CASPT2, relative energies (kcal/mol) of the transition structures, the intermediates and the products in the ring expansion of the $^1A_2$ state of phenylnitrene and of phenylphosphinidene.

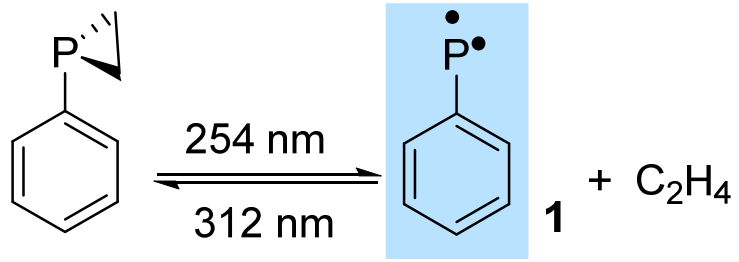
*Galbraith et al., JACS, 2002,124, 11669.*

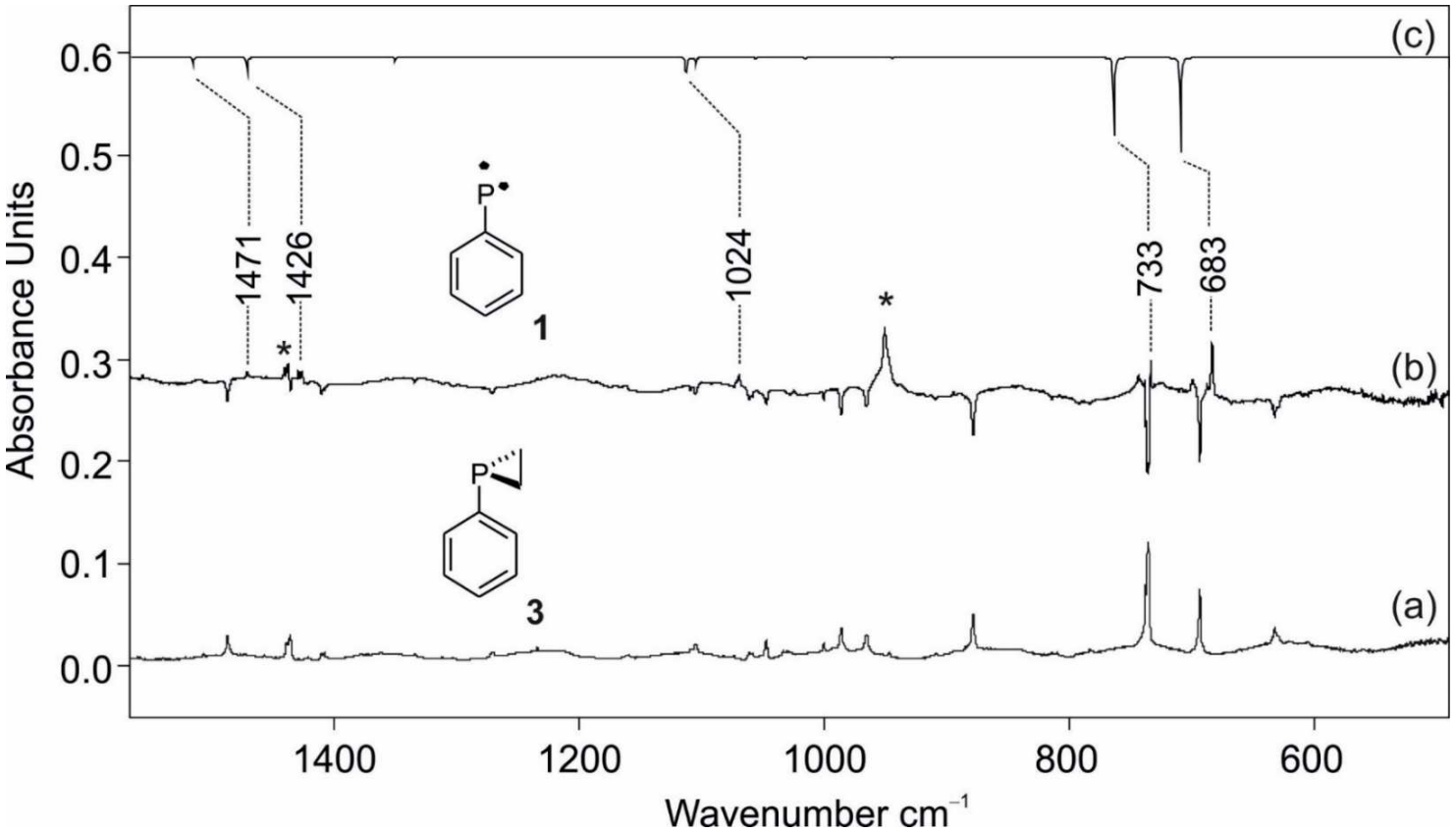
# Photochemical Reactions of Triplet Phenylphosphinidene




*(a) Mardyukov, Niedek & Schreiner, JACS, **2017,** 139, 5019-5022**.** (b) Mardyukov & Niedek, ChemComm., **2018**, 54(97),13694-13697.*

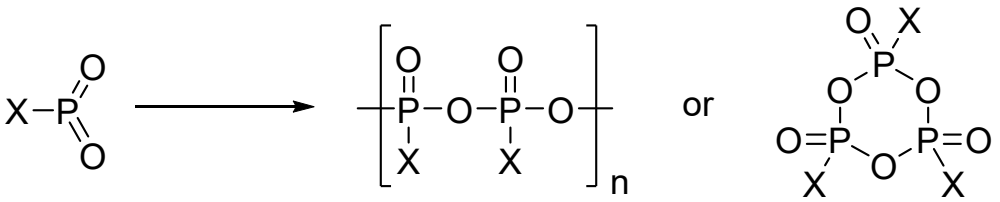
# Preparation and Isolation of Triplet Phenylphosphinidene




*Mardyukov, Niedek & Schreiner, JACS*, **2017,** 139, 5019-5022**.**

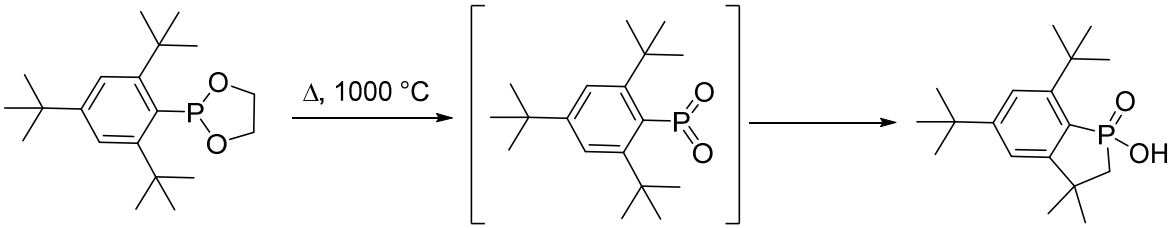
# Known Dioxophosphoranes ($RPO_2$)



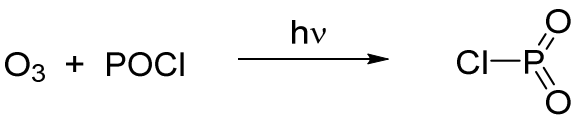
or



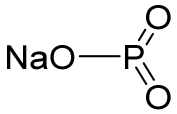
Quin, L. D. *Coord. Chem. Rev.* **1994**, *137*, 525



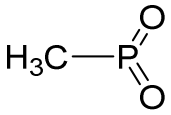

Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 3134




Ahlrichs, et al., *J. Am. Chem. Soc.* **1986**, *108*, 3596.



Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1979**, 1465.



Heydorn et al., Chem Phys Lett, **2003**, 584.

# Reaction of Phenylphosphinidene with $^3P$-$O_2$

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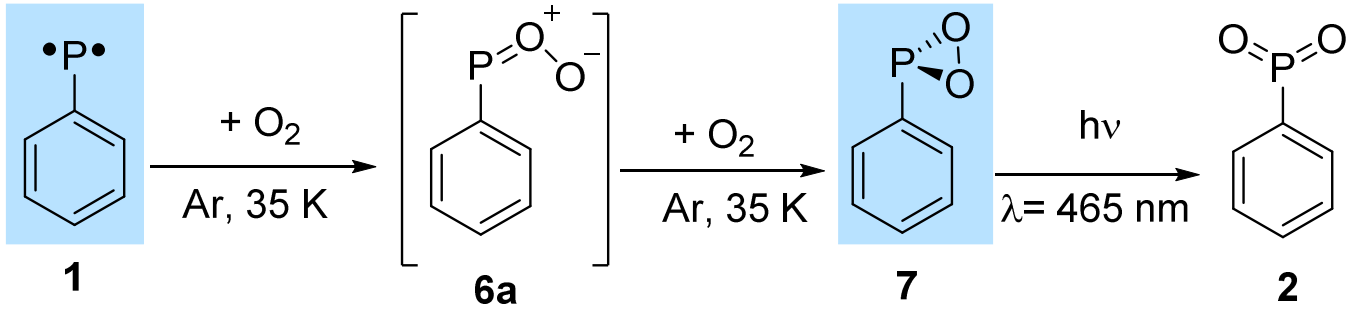


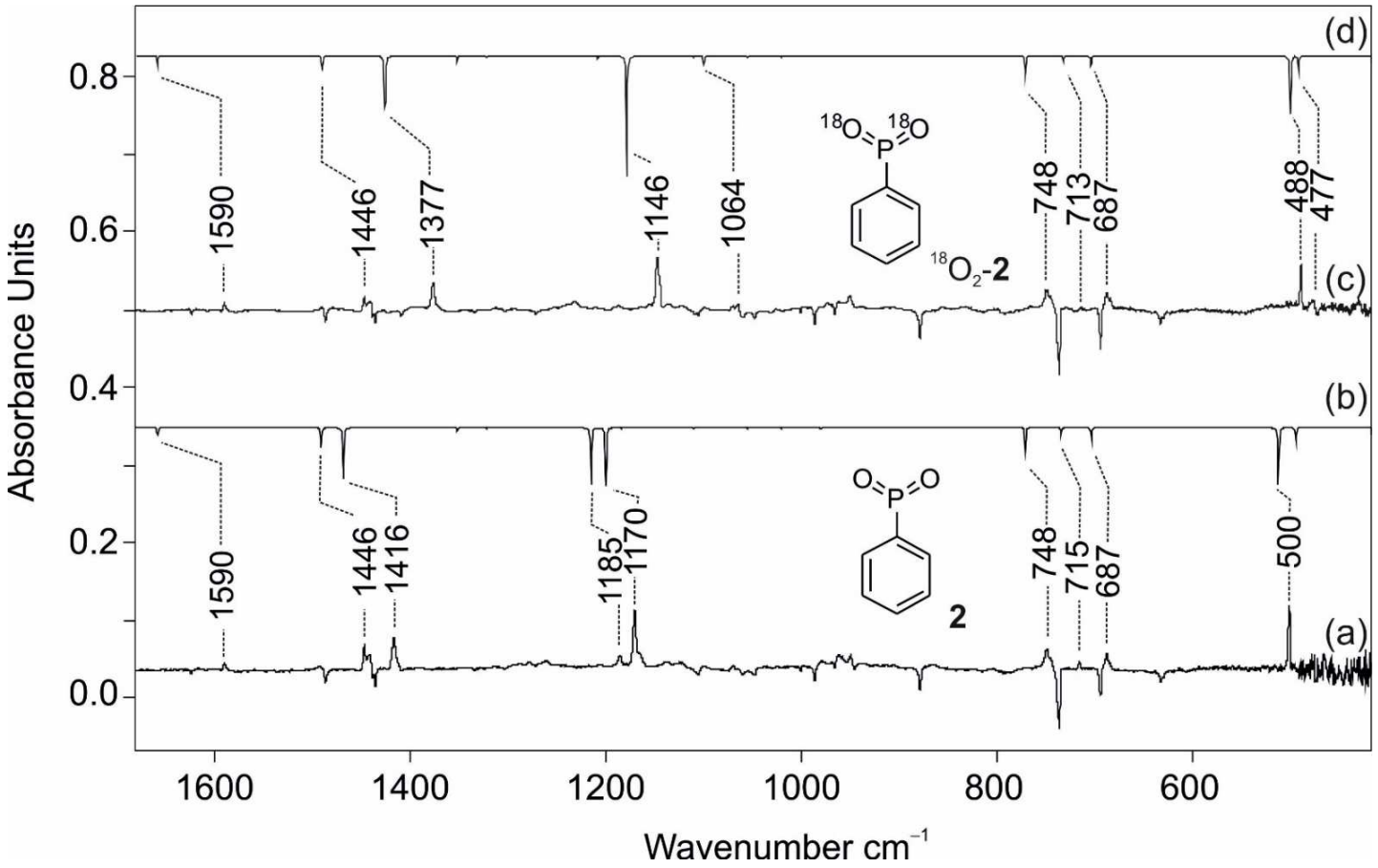

# Reaction of Phenylphosphinidene with Carbon Monoxide (CO)

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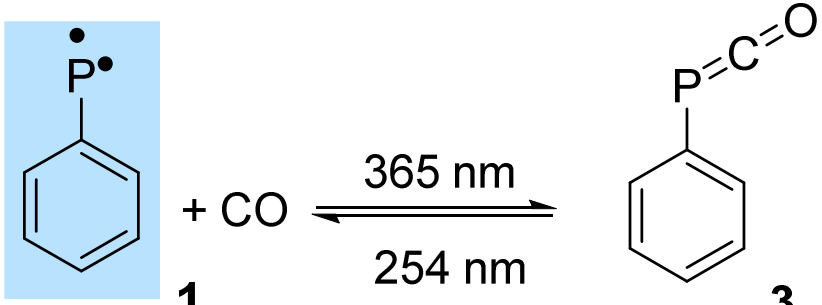
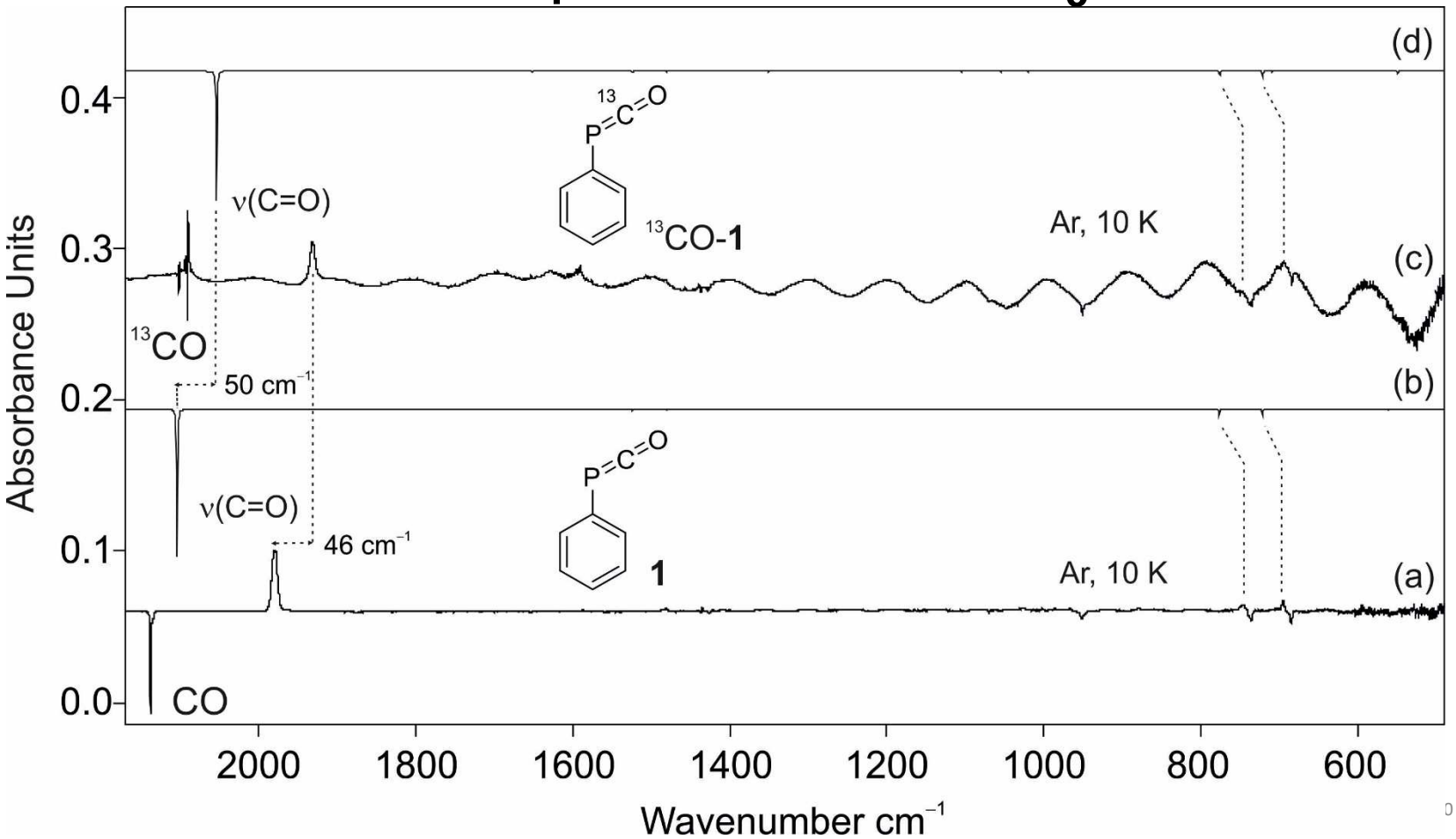
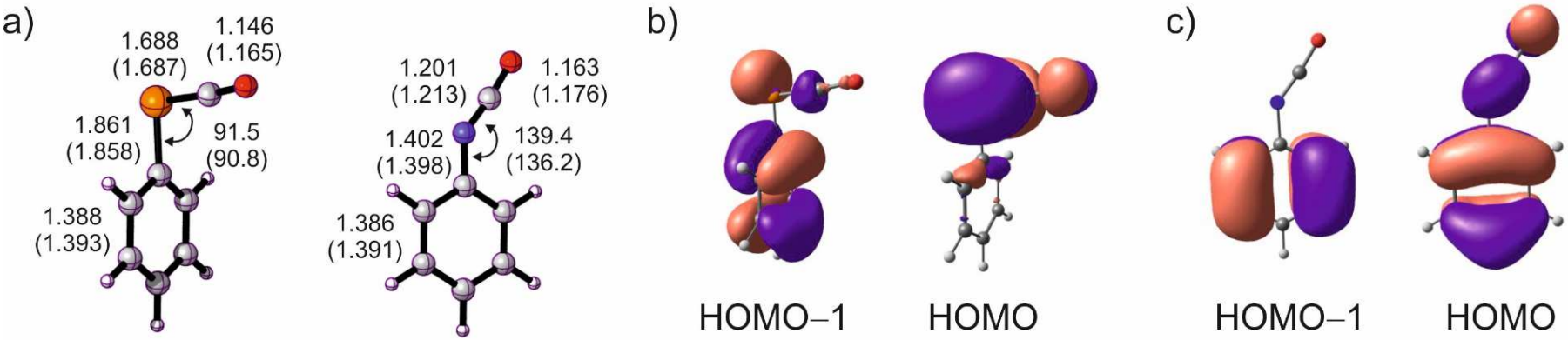



**1** **3**



# Selected Bond Lengths and Molecular Orbitals





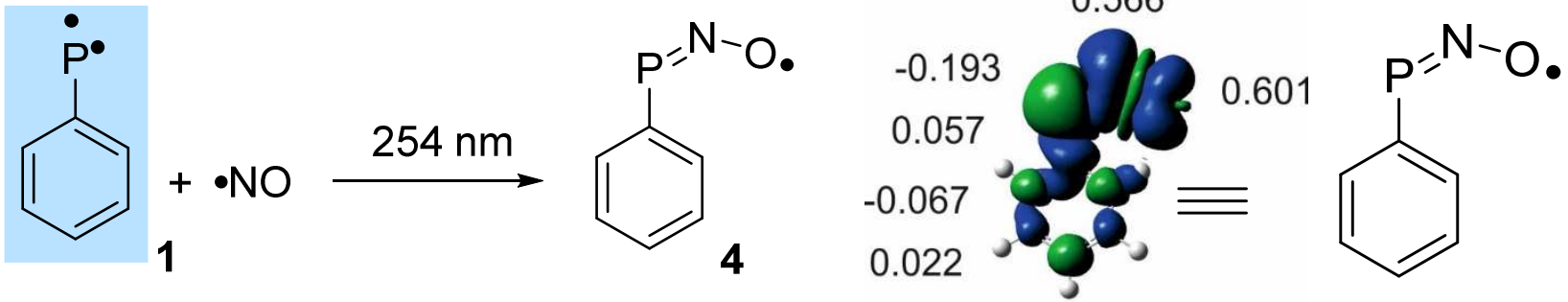

Selected bond lengths (Å) at the M06-2X/6-311++G(2d,2p) level. The values in parentheses at MP2/cc-pVTZ.

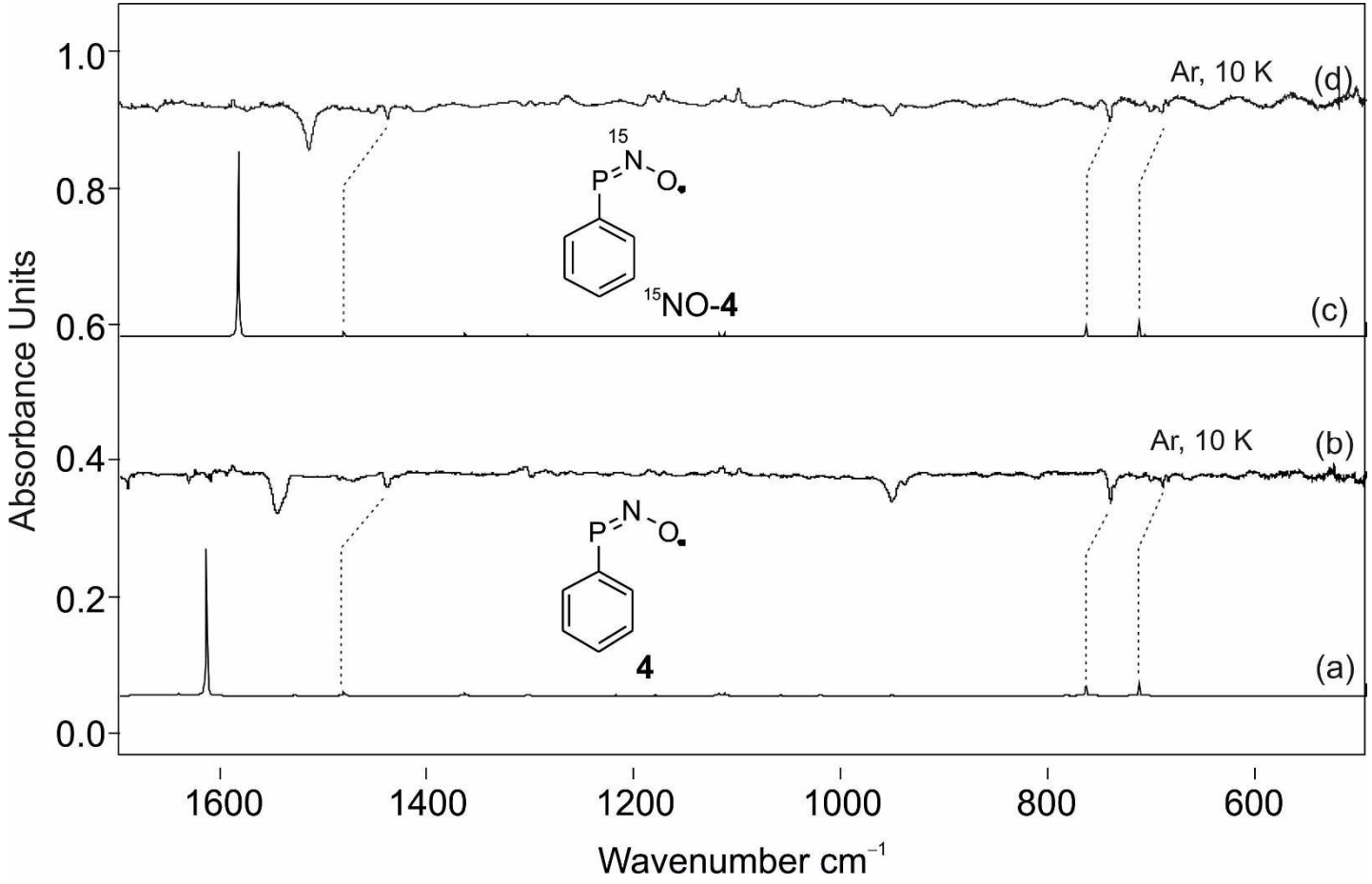
(b) Molecular orbitals computed at the M06-2X/6-311++G(2d,2p) level. (c) Molecular orbitals computed at the M06-2X/6-311++G(2d,2p) level

*Mardyukov & Niedek, ChemComm., **2018**, 54(97),13694-13697.*

# Reaction of Phenylphosphinidene with •NO

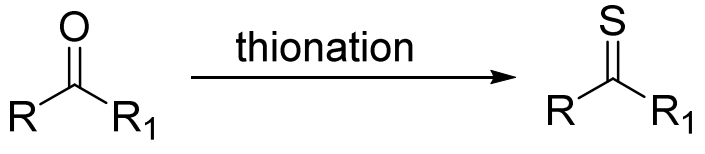


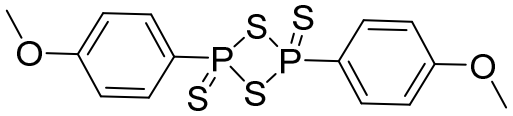


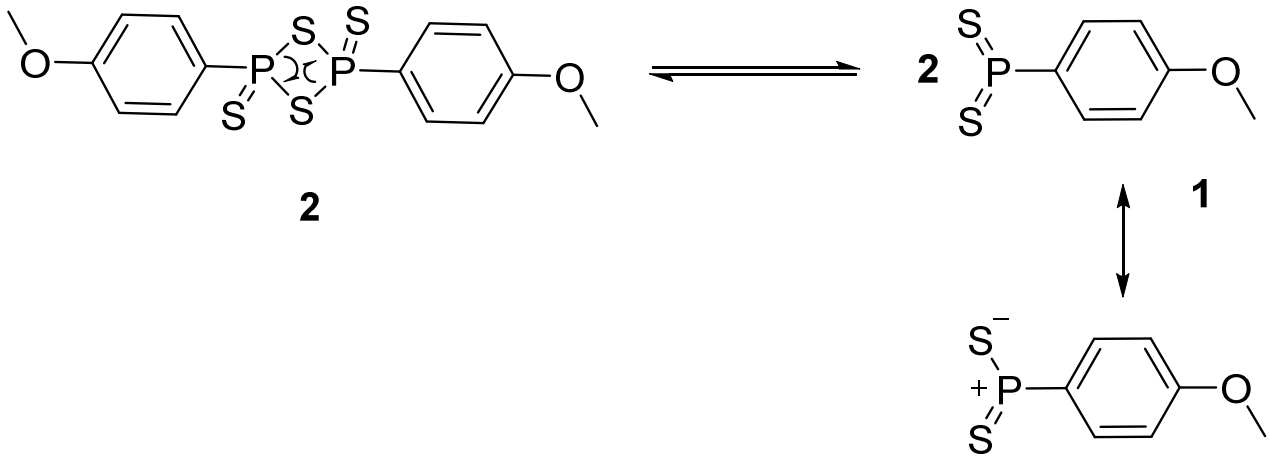
# Unravelling Lawesson's Reagent – The Structure of Monomeric (4-Methoxyphenyl)phosphine Disulfide

# Thionation Reagent and Dissociation Mechanisms of Lawesson's Reagent



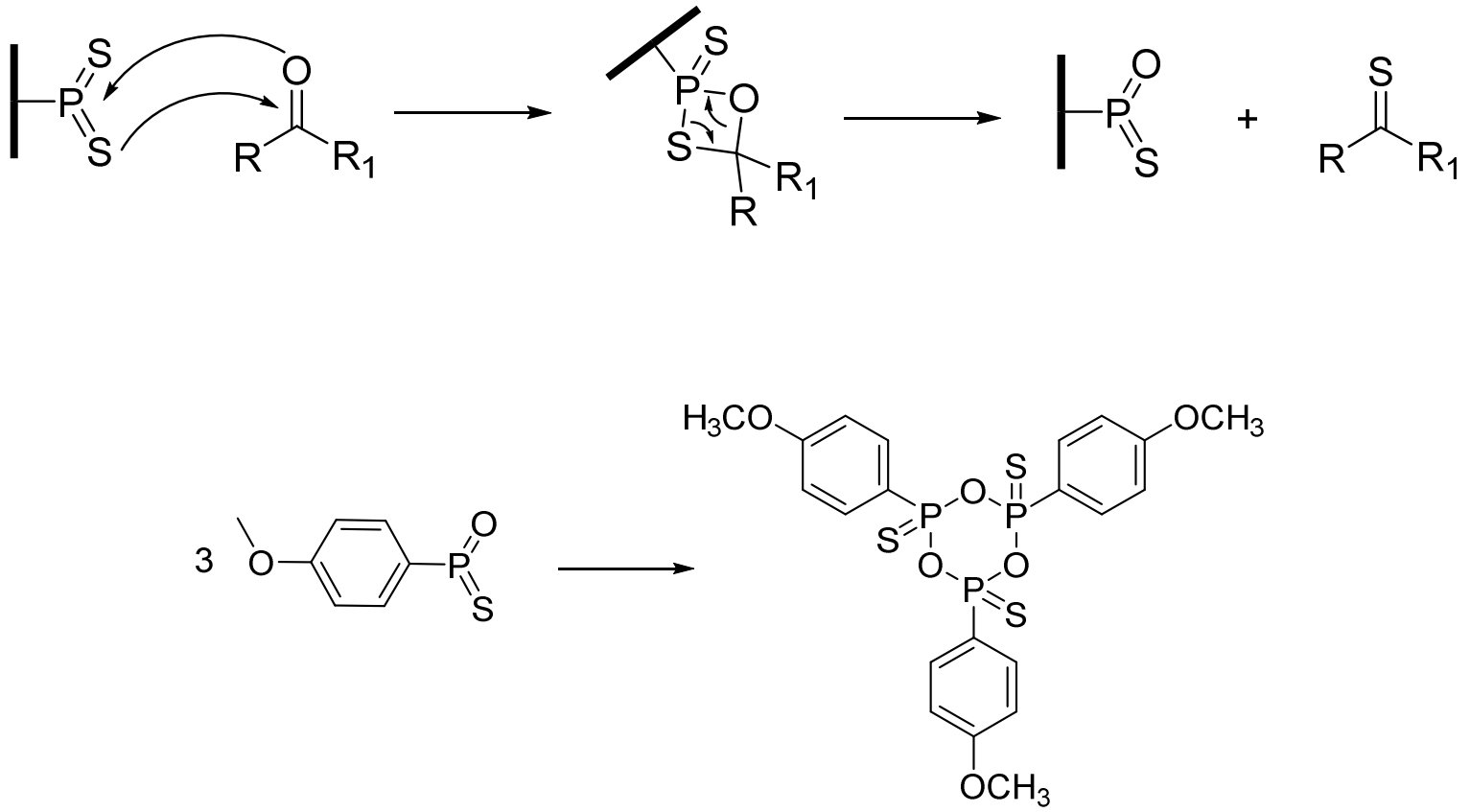




Lawesson's Reagent




*Jesberger et al., Synthesis, 2003, 13, 1929–1958,*

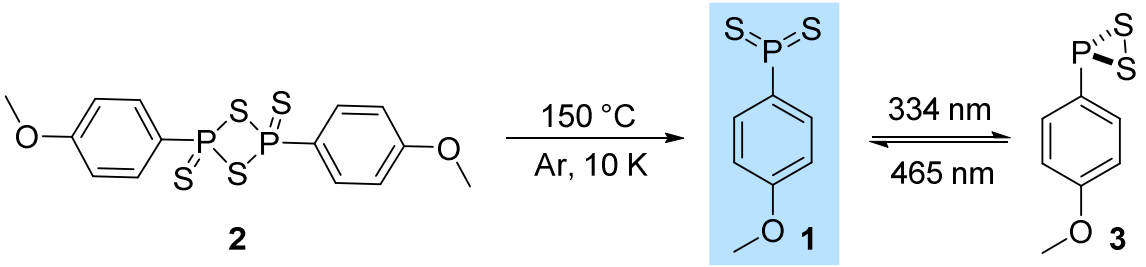
# Thionation Mechanism / Formation of the Side Product

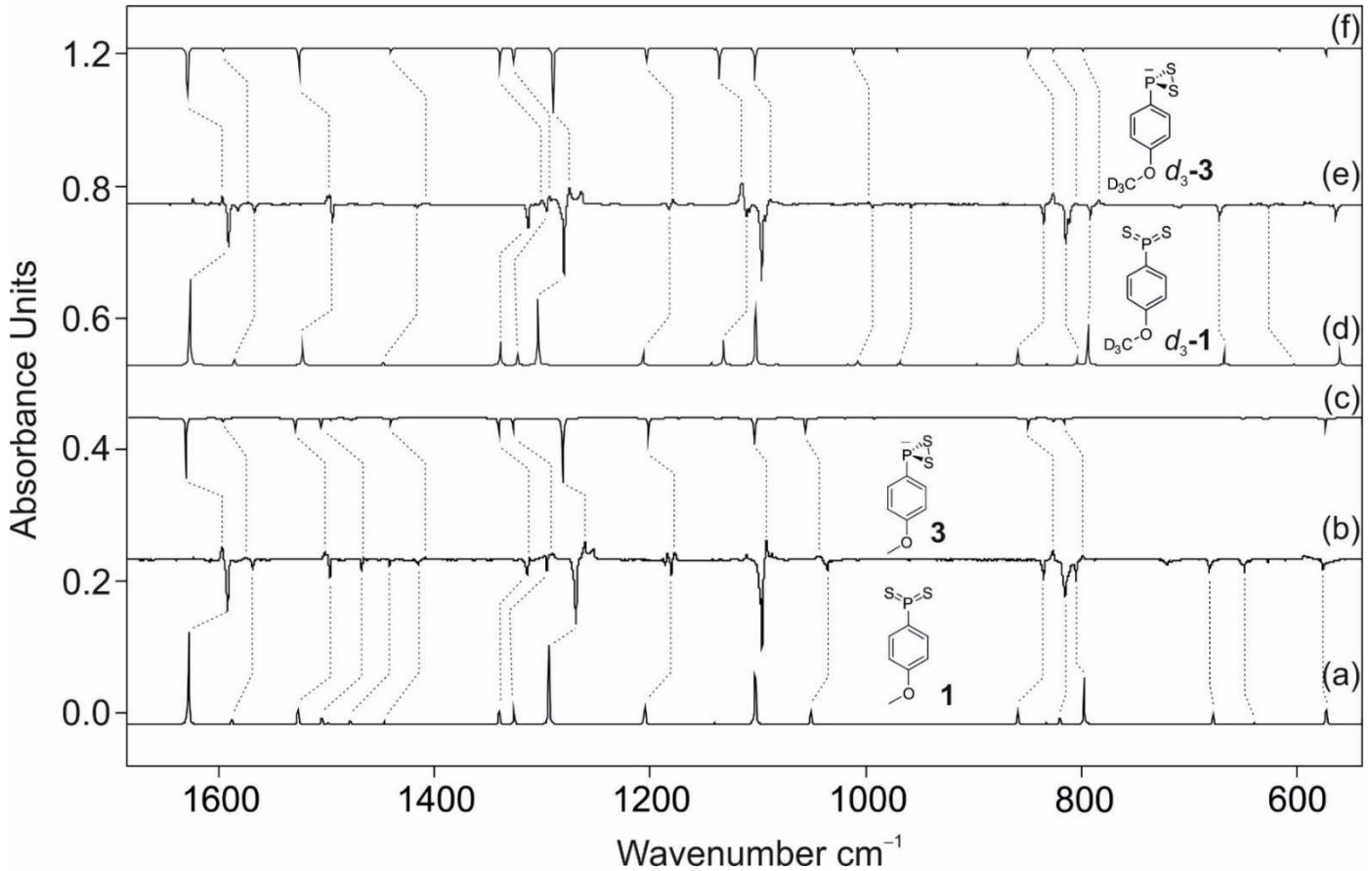



Jesberger et al., Synthesis, 2003, 13, 1929–1958,

# IR Spectra - Matrix Isolation

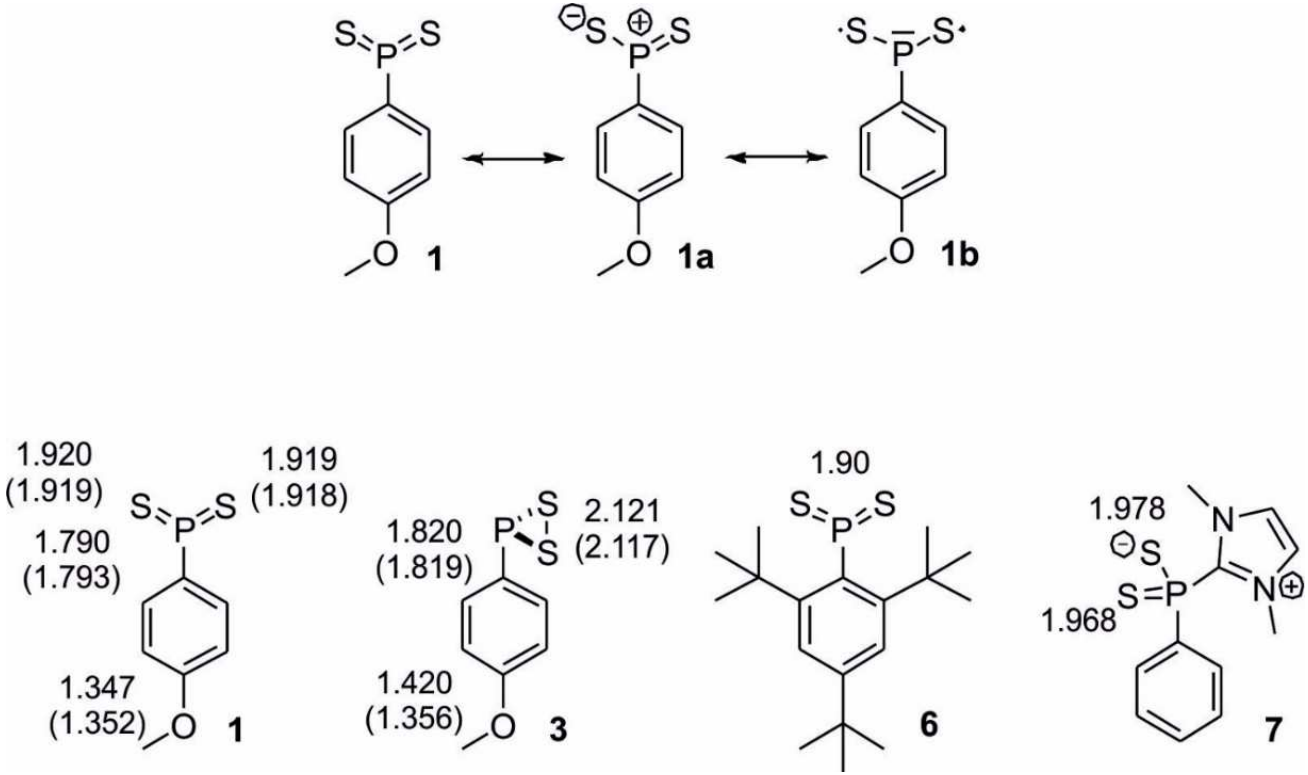




# Resonance Structures and Bond Lengths

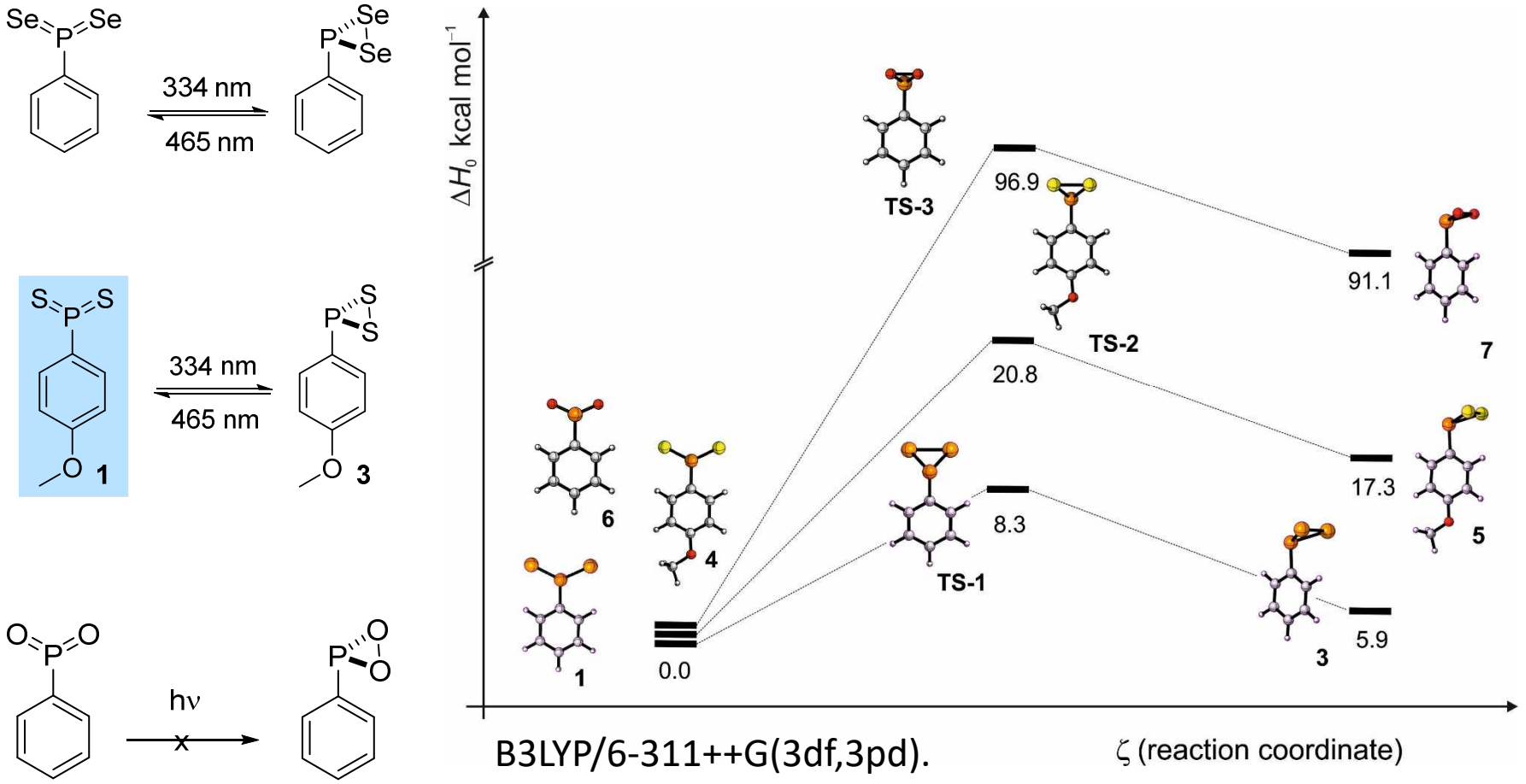





B3LYP/6-311++G(3df,3pd)
MP2/cc-pVTZ.

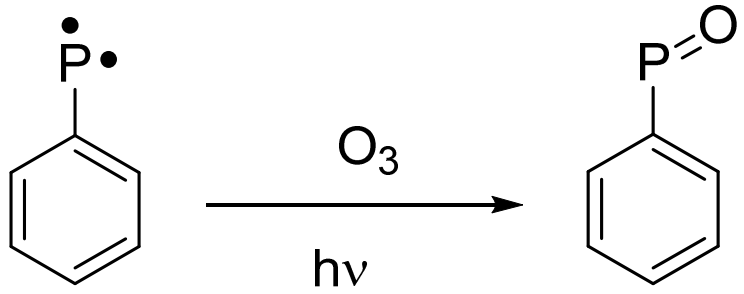
*(a) D. Bockfeld, et al., Eur. J. Inorg. Chem.,* ***2017****, 2017, 3452-3458. (b) R. Appel et al., Angew. Chem.,* ***1983****, 95, 1008-1009. (c) Mardyukov, Niedek, Schreiner, ChemComm,* ***2018.*** *54, 2715--2718.*

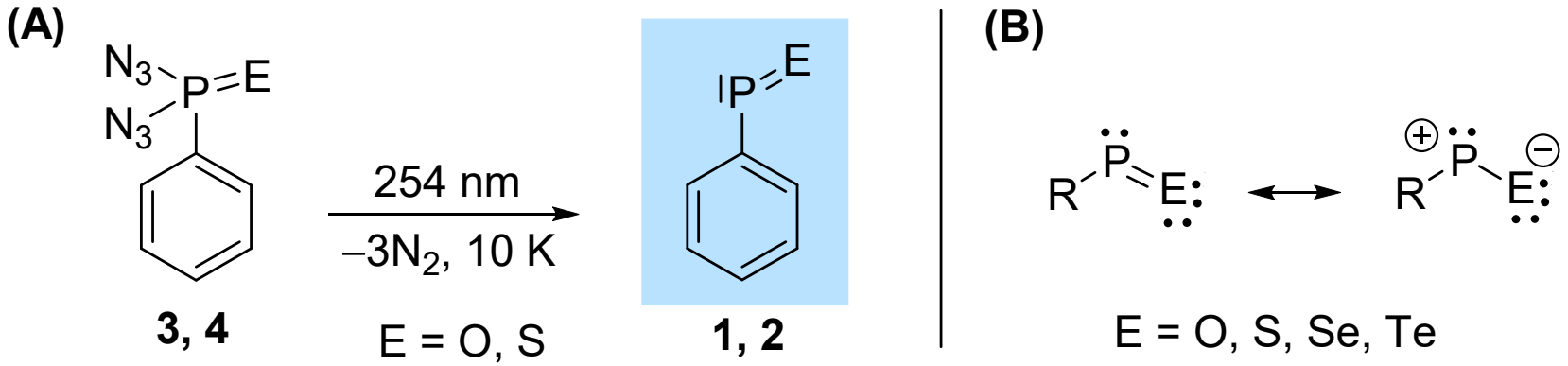
# Potential Energy Diagram: Isomerization Pathways




*Mardyukov, Niedek & Schreiner*, *ChemComm*, 2018, 54, 2715--2718. *Mardyukov, Keul & Schreiner*, *Eur. J. Org. Chem*, **2019**, 387-390.

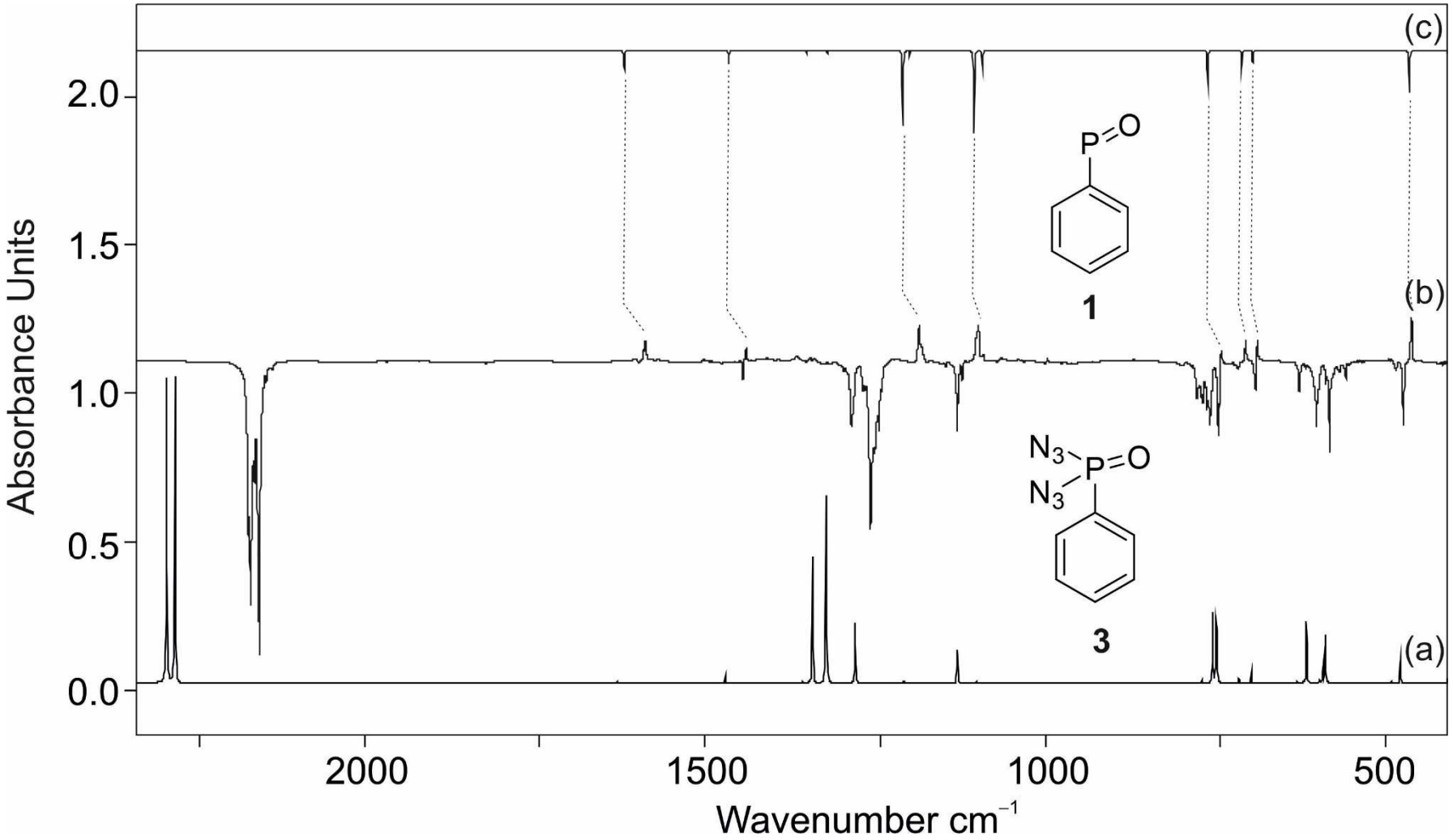
# Phosphinidene Oxide



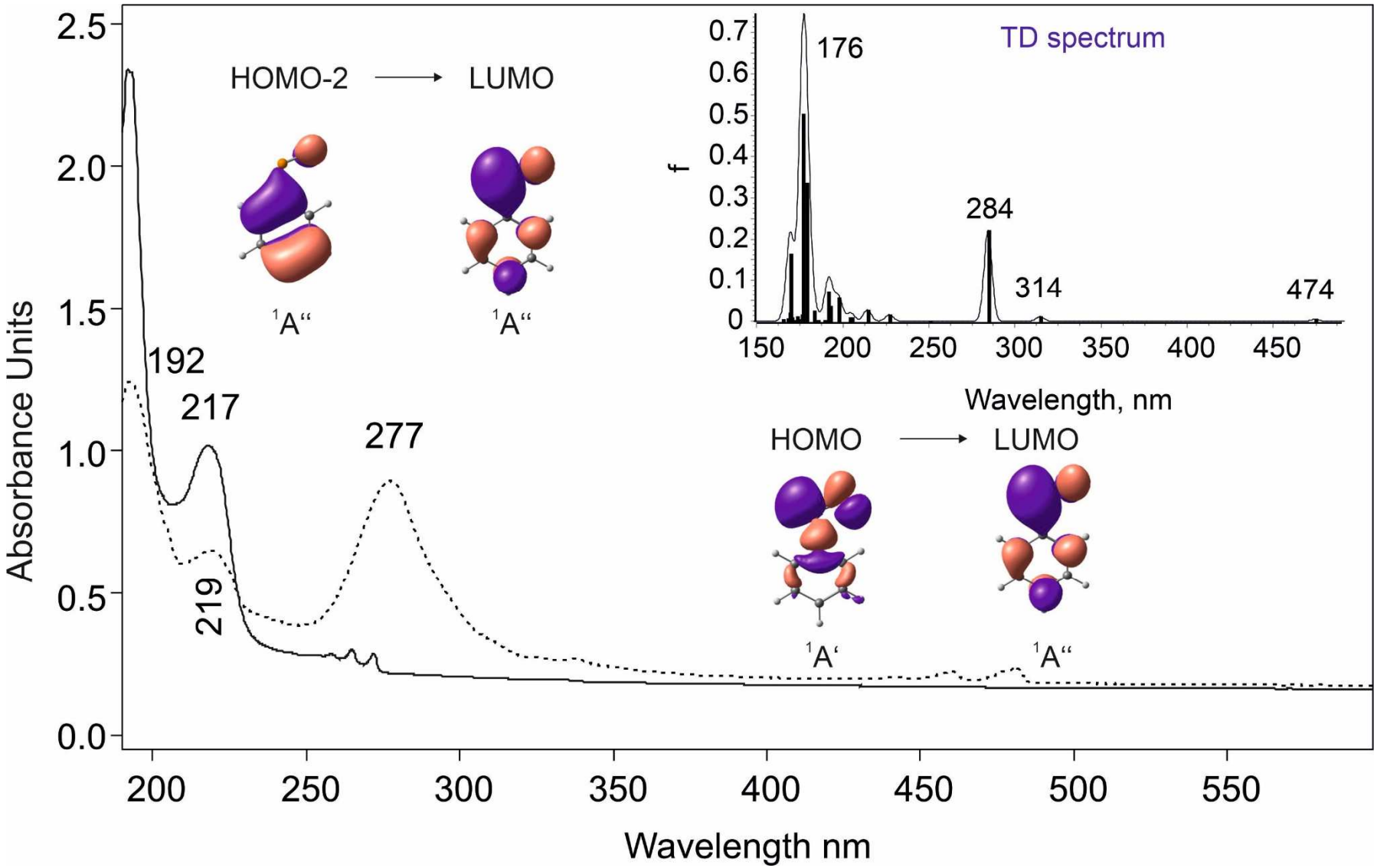

Mardyukov, Keul, Schreiner, Angew. Chem. Int. Ed., **2020**, 59, 12445 –12449

# IR Spectra - Matrix Isolation



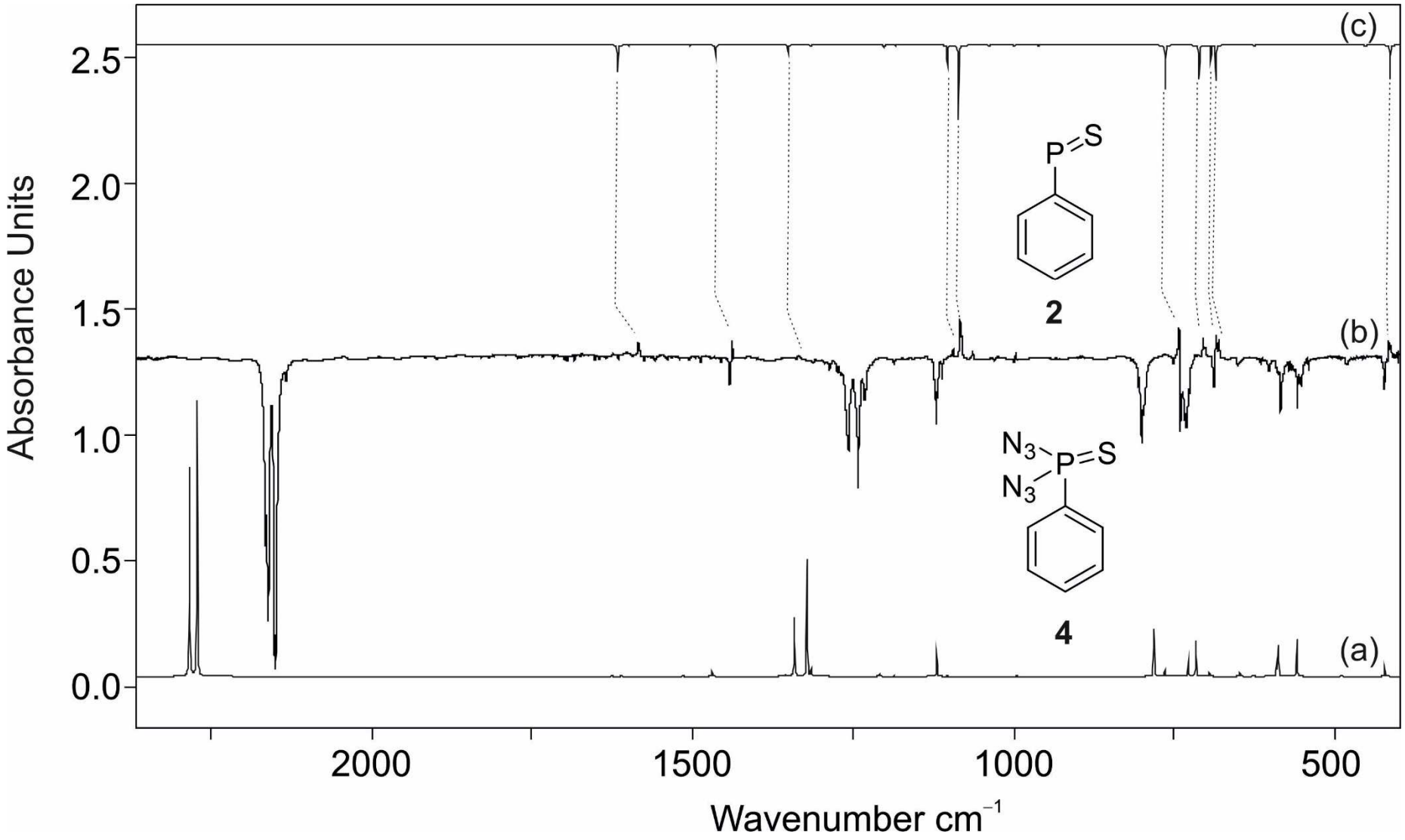
# UV/Vis Spectra - Matrix Isolation



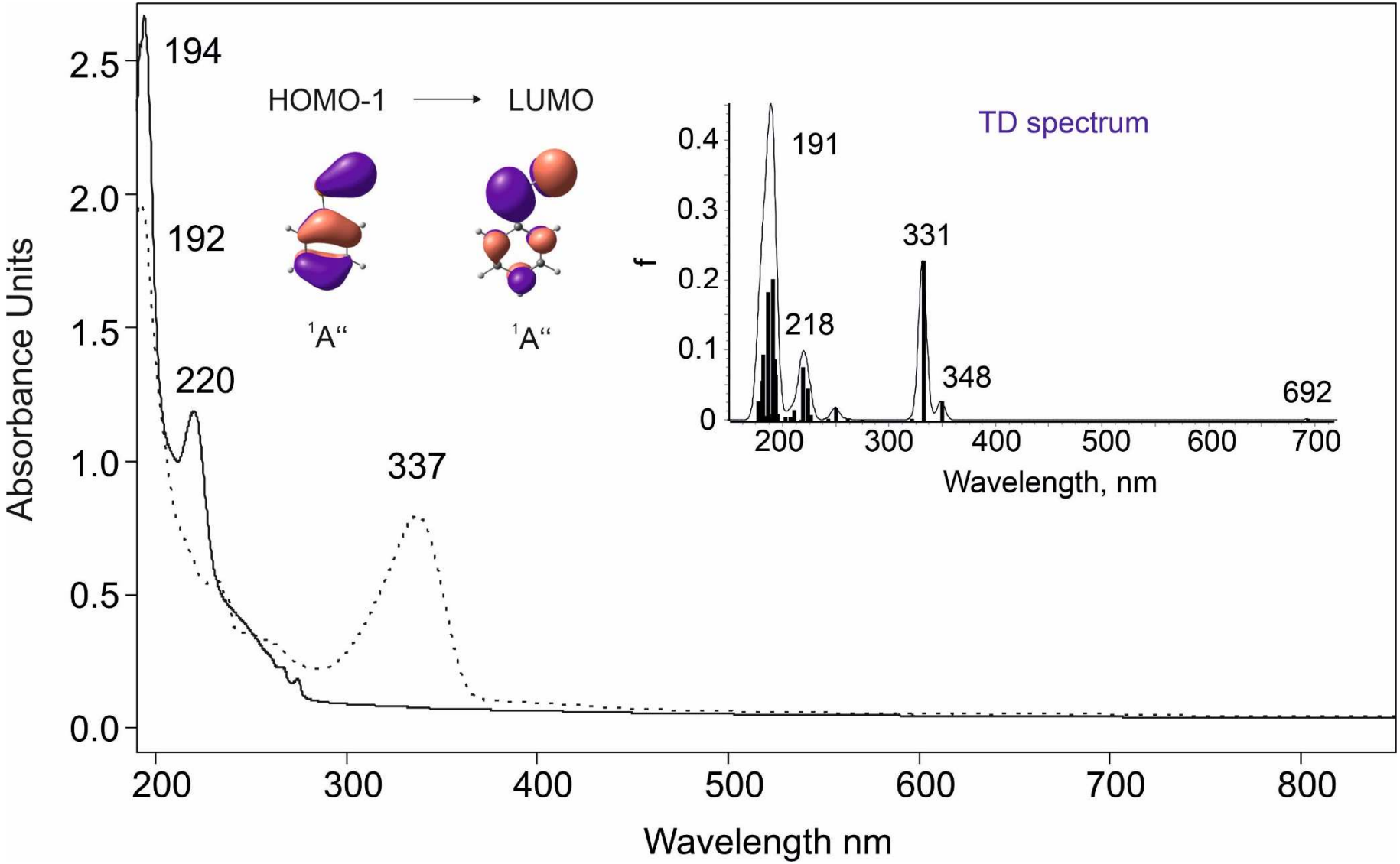


# IR Spectra - Matrix Isolation

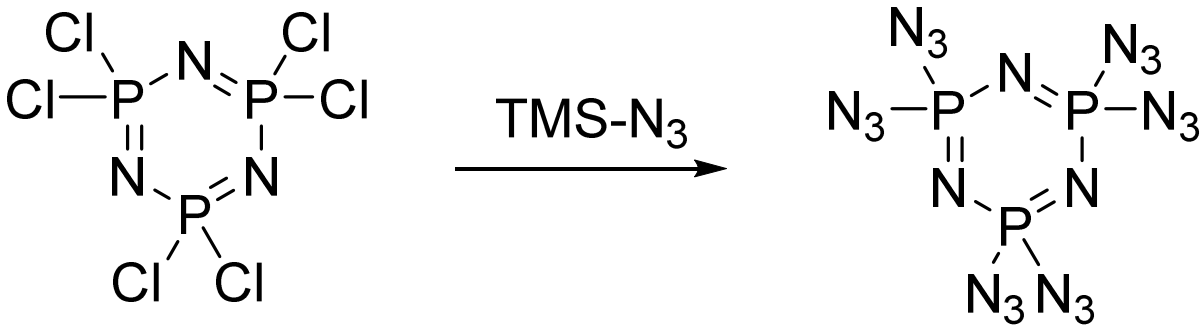




# UV/Vis Spectra - Matrix Isolation



# Synthesis of $P_3N_{21}$




Angewandte Chemie

**Phosphorus Nitrides**

DOI: 10.1002/anie.200601670

## The First Structural Characterization of a Binary P–N Molecule: The Highly Energetic Compound $P_3N_{21}$**

*Michael Göbel, Konstantin Karaghiosoff, and Thomas M. Klapötke**

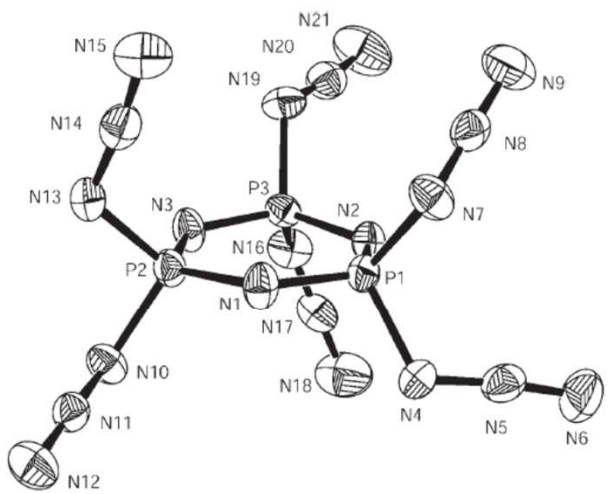
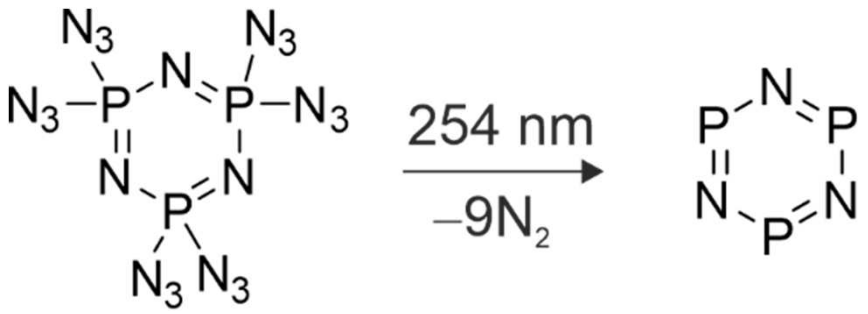
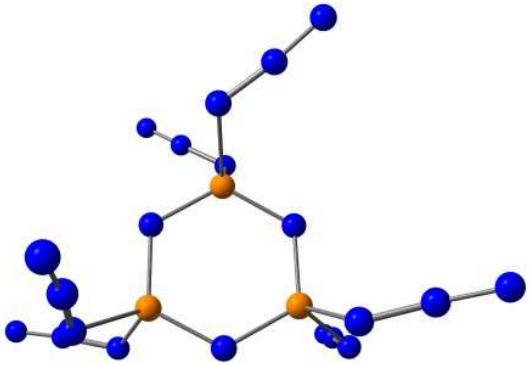


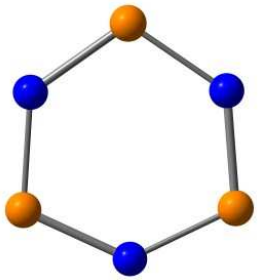

*Figure 3.* ORTEP representation of the molecular structure of $P_3N_{21}$; thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: P1–N1 1.558(2), P1–N2 1.576(2), P1–N4 1.666(2), P1–N7 1.671(2), N4–N5 1.218(3), N5–N6 1.117(3), N7–N8 1.203(3), N8–N9 1.114(3); N1-P1-N2 118.2(1), P1-N1-P2 122.1(1), N4-N5-N6

# Photochemical Synthesis of Cyclotriphosphazene ($P_3N_3$)




# Computed Structures of $P_3N_{21}$ and $P_3N_3$





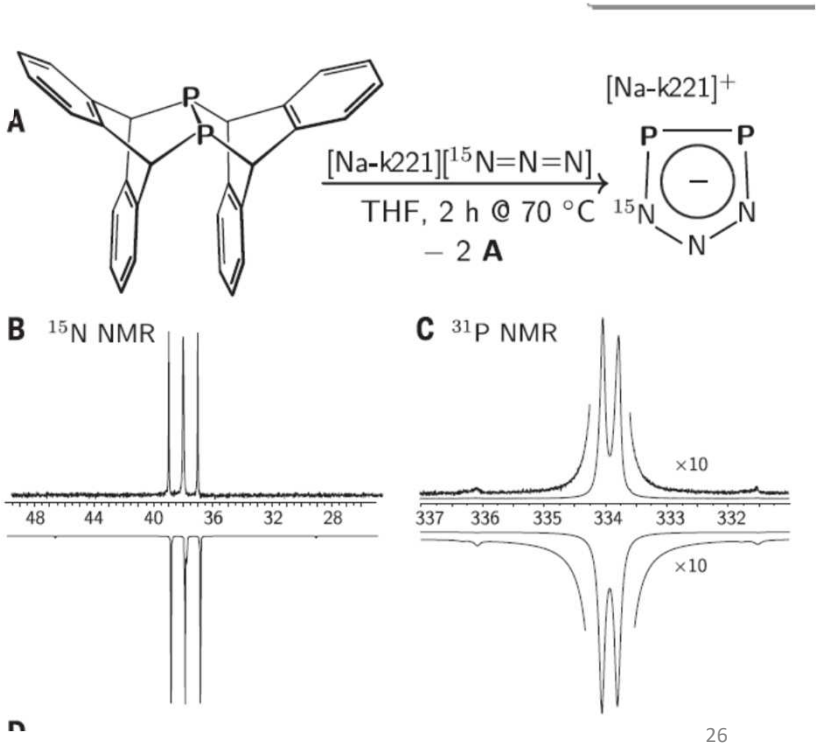
Blue – nitrogen; orange – phosphorus

INORGANIC CHEMISTRY

# Synthesis and characterization of $P_2N_3^-$: An aromatic ion composed of phosphorus and nitrogen

Alexandra Velian and Christopher C. Cummins*

Aromaticity is predominantly associated with carbon-rich compounds but can also occur in all-inorganic ones. We report the synthesis of the diphosphatriazolate anion, a rare example of a planar aromatic inorganic species. Treatment of azide ($N_3^-$) in tetrahydrofuran solution with $P_2A_2$ (A = $C_{14}H_{10}$), a source of $P_2$, produced $P_2N_3^-$, which we isolated as its [Na-kryptofix-221]$^+$ salt in 22% yield and characterized by single-crystal x-ray diffraction. Salts [Na-kryptofix-221] [$P_2N_3$] and [Na-kryptofix-221] [$P_2{}^{15}NN_2$] were analyzed by infrared and Raman spectroscopy, $^{15}N$ and $^{31}P$ nuclear magnetic resonance spectroscopy, and mass spectrometry. The formation of the $P_2N_3^-$ anion was investigated using density functional theory, and its aromatic character was confirmed by NICS (nucleus-independent chemical shift) and QTAIM (quantum theory of atoms in molecules) methods.



CHEMISTRY

# The elusive cyclotriphosphazene molecule and its Dewar benzene–type valence isomer ($P_3N_3$)

**Cheng Zhu[1,2]*, André K. Eckhardt[3,*†], Alexandre Bergantini[1,2‡], Santosh K. Singh[1,2], Peter R. Schreiner[3§], Ralf I. Kaiser[1,2§]**

Although the chemistry of phosphorus and nitrogen has fascinated chemists for more than 350 years, the Hückel aromatic cyclotriphosphazene ($P_3N_3$, **2**) molecule—a key molecular building block in phosphorus chemistry—has remained elusive. Here, we report a facile, versatile pathway producing cyclotriphosphazene and its Dewar benzene–type isomer ($P_3N_3$, **5**) in ammonia-phosphine ices at 5 K exposed to ionizing radiation. Both isomers were detected in the gas phase upon sublimation via photoionization reflectron time-of-flight mass spectrometry and discriminated via isomer-selective photochemistry. Our findings provide a fundamental framework to explore the preparation of inorganic, isovalent species of benzene ($C_6H_6$) by formally replacing the C—H moieties alternatingly through phosphorus and nitrogen atoms, thus advancing our perception of the chemical bonding of phosphorus systems.



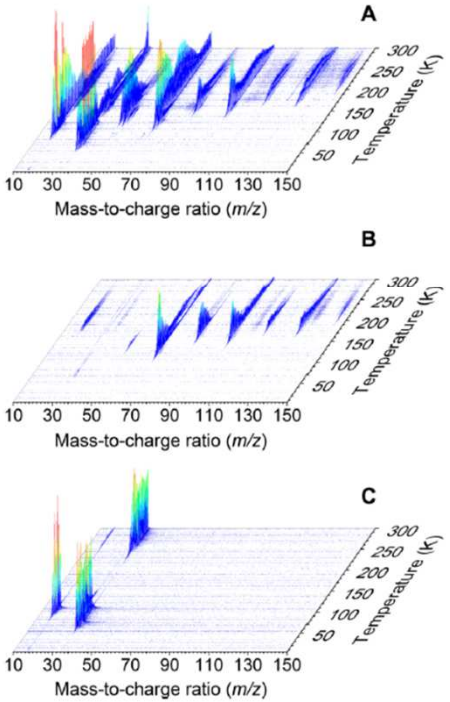



**Fig. 3. PI-ReTOF-MS data during the TPD phase of the phosphine ($PH_3$) and ammonia ($NH_3$) ice mixtures.** (**A**) Electron processed ice, PE = 10.49 eV.

ACS OMEGA

Article

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# Computational Assessment of an Elusive Aromatic $N_3P_3$ Molecule

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*Supporting Information*

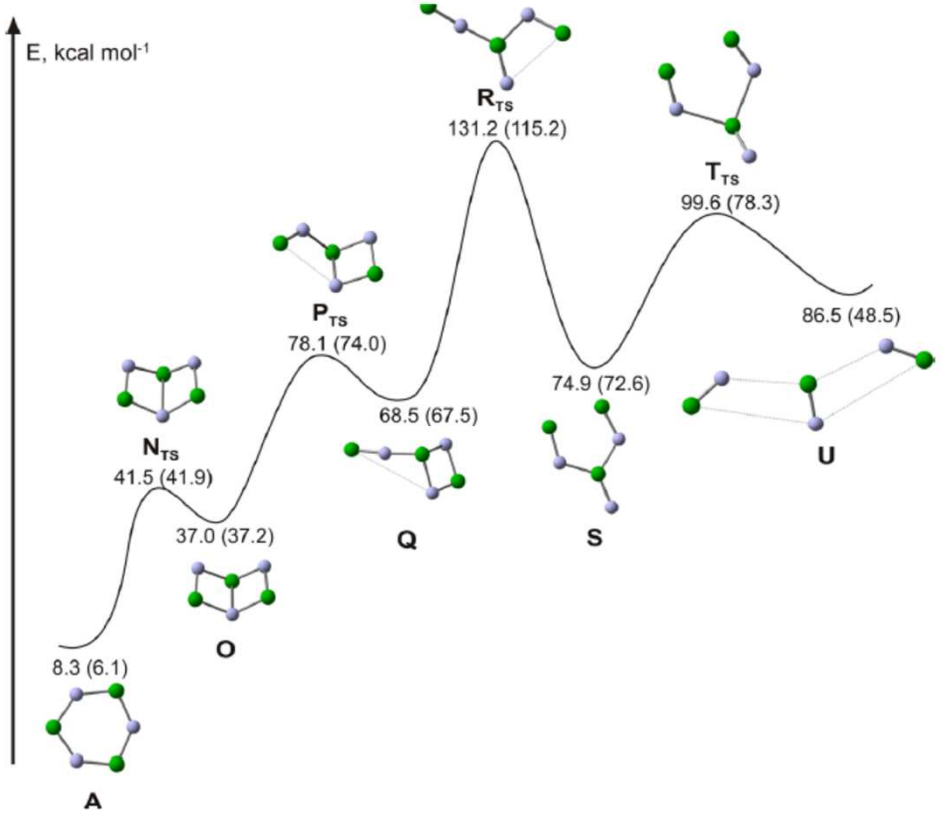
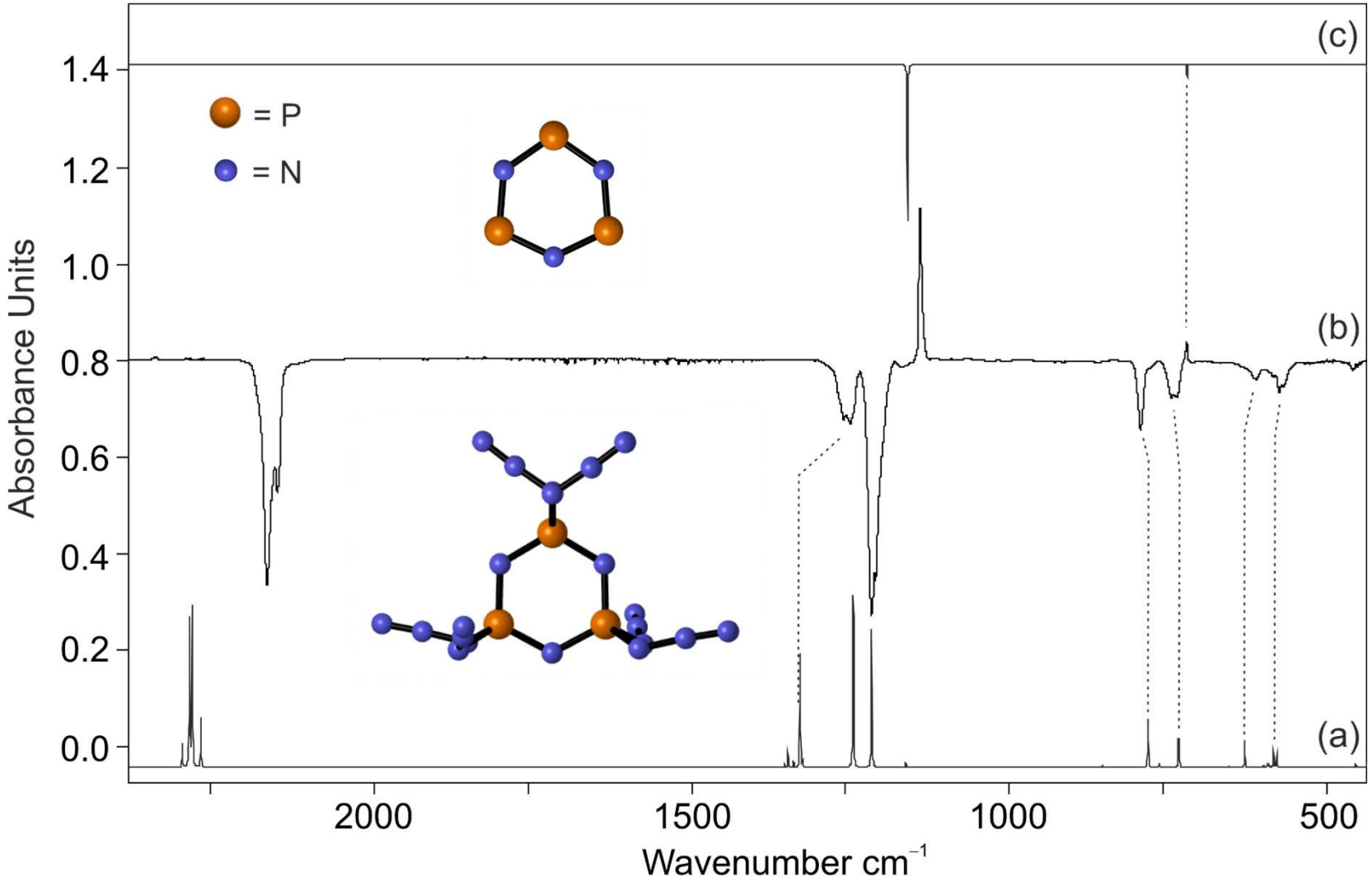


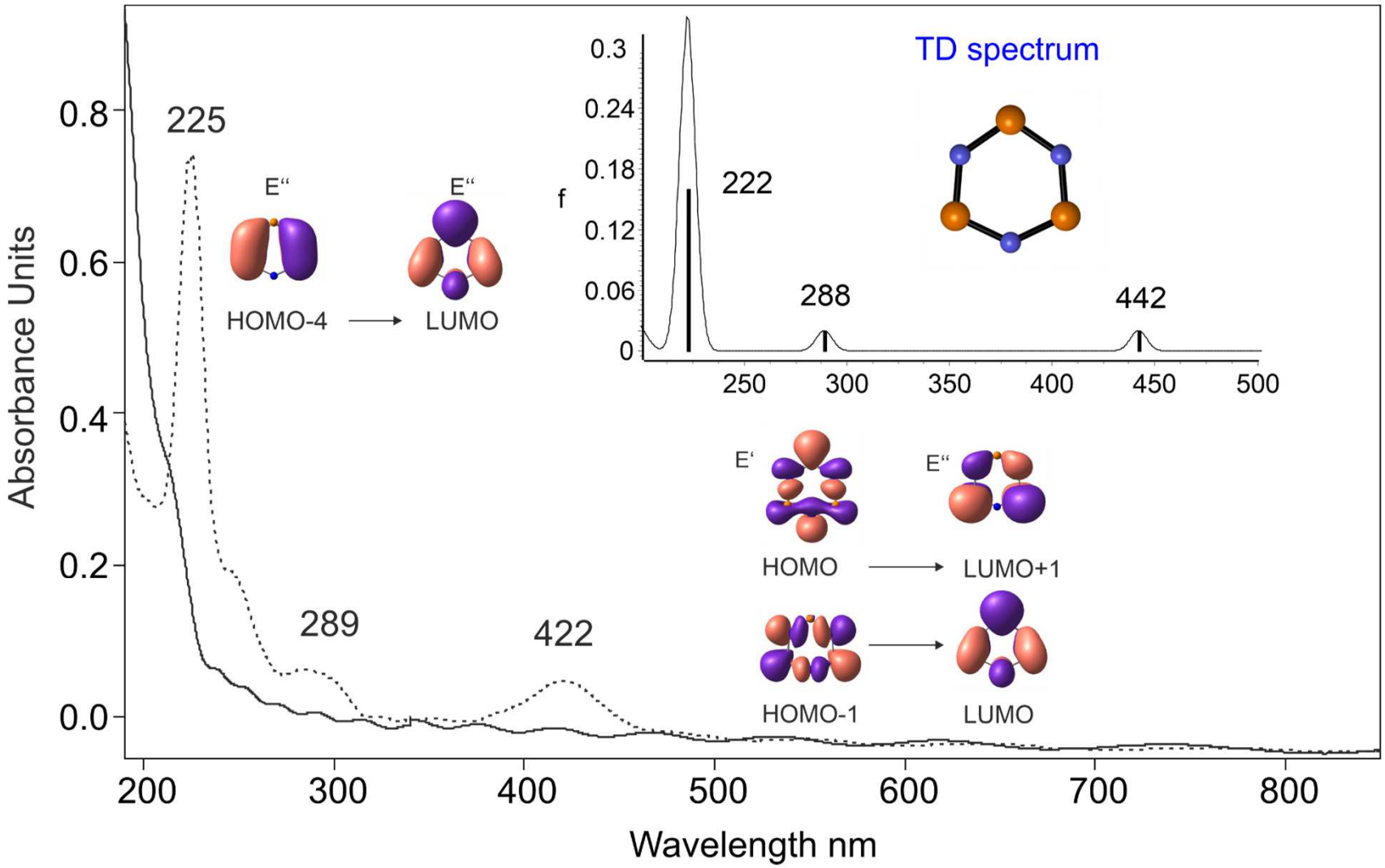

**Figure 4.** Mechanism of dissociation of hexagon-like structure **2** (A) into three PN molecules, according to the PBE0/6-311+G*+ZPE calculations. Data on single-point calculations performed by using CCSD(T)/6-311+G(d) are shown in brackets.

# Matrix Isolation – IR Spectroscopy



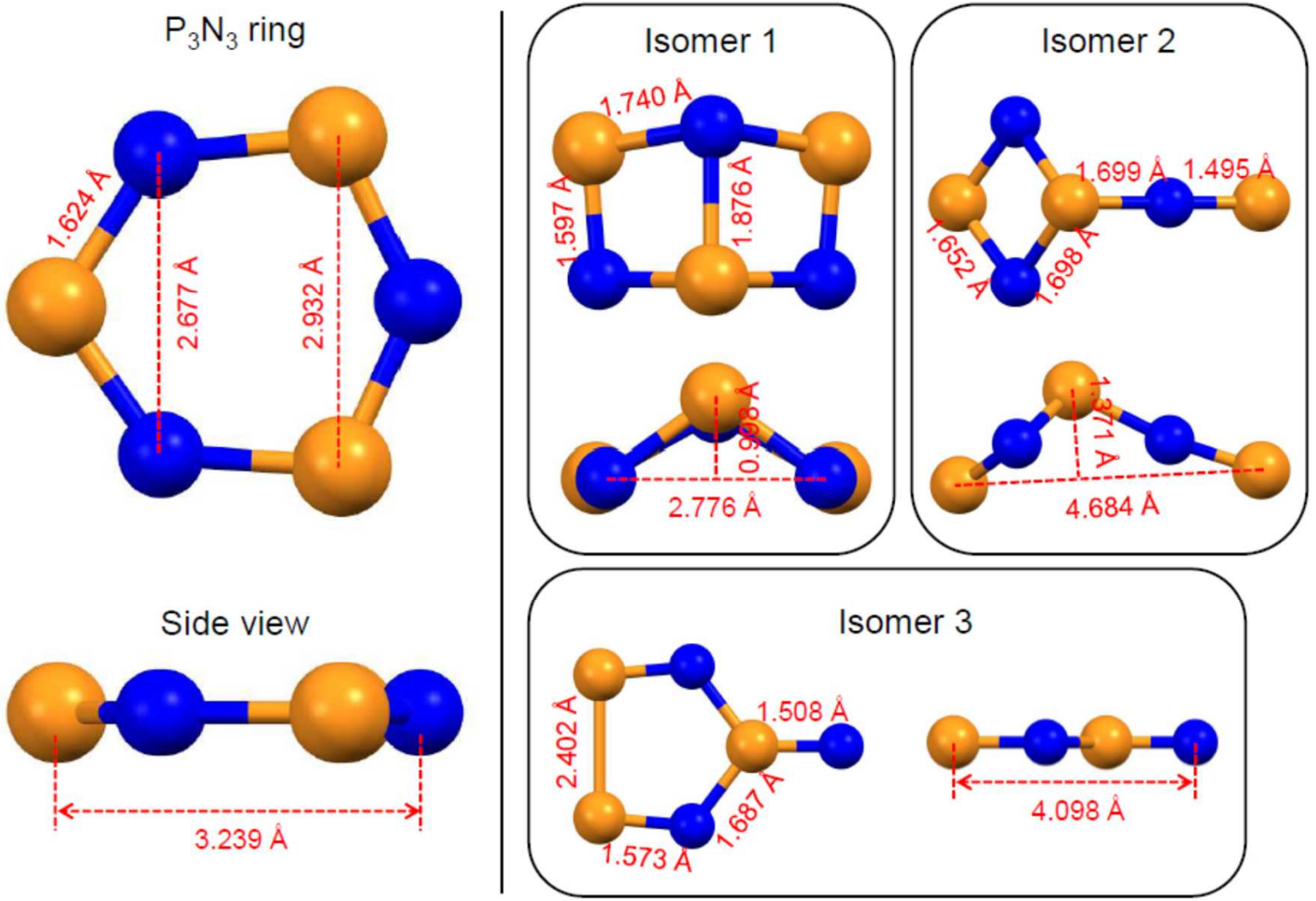

(a) IR spectrum of $\mathbf{P_3N_{21}}$ computed at B3LYP/6-311++G(3df,3pd) (unscaled). (b) IR difference spectra showing the photochemistry of $\mathbf{P_3N_{21}}$ after irradiation with $\lambda$ = 254 nm in argon at 10 K. Downward bands assigned to $\mathbf{P_3N_{21}}$ disappear while upward bands assigned to $\mathbf{P_3N_3}$ after 20 min irradiation time. (c) IR spectrum of $\mathbf{P_3N_3}$ computed at at B3LYP/6-311++G(3df,3pd) (unscaled).

# Matrix Isolation - UV/Vis Spectroscopy

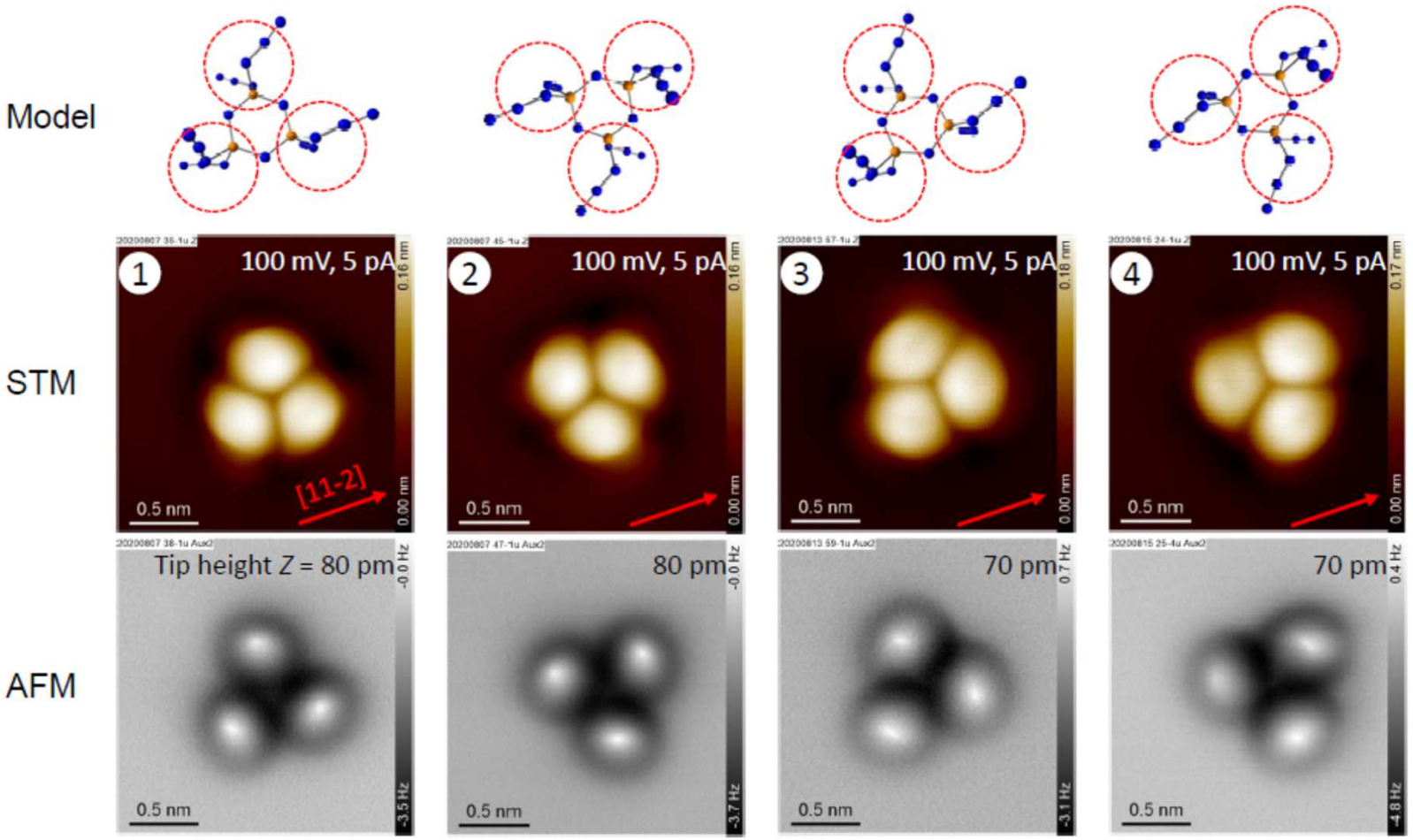



Solid: UV/Vis spectrum of $\mathbf{P_3N_{21}}$ isolated at 10 K in Ar. Dashed: UV/Vis spectrum of $\mathbf{P_3N_3}$ at 10 K; the photochemistry of $\mathbf{P_3N_{21}}$ after irradiation at $\lambda$ = 254 nm in Ar at 10 K. Inset: Computed [TD-B3LYP/6-311++G(3df,3pd)] spectrum of $\mathbf{P_3N_3}$.

# Computed Structures



# High-resolution STM & AFM images of single $P_3N_{21}$ molecules




**Note:** The threefold symmetry of $P_3N_{21}$ is revealed by both STM and AFM images. The diverging $-N_3$ groups are imaged as three bright protrusions. The models in the top row are calculated in the gas phase, so they do not exactly correspond to the adsorbed ones.

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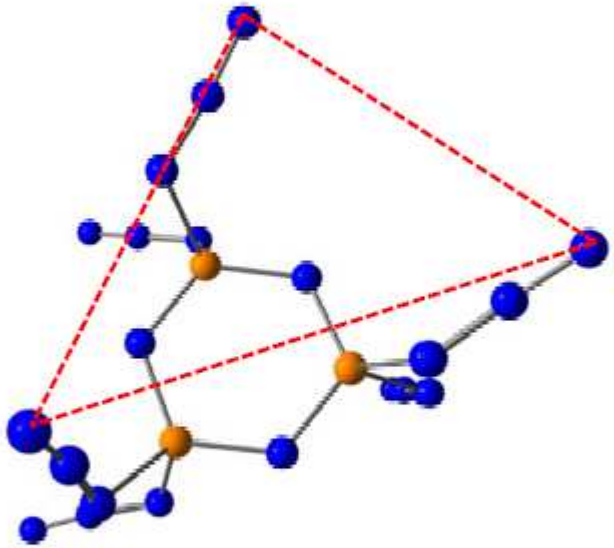
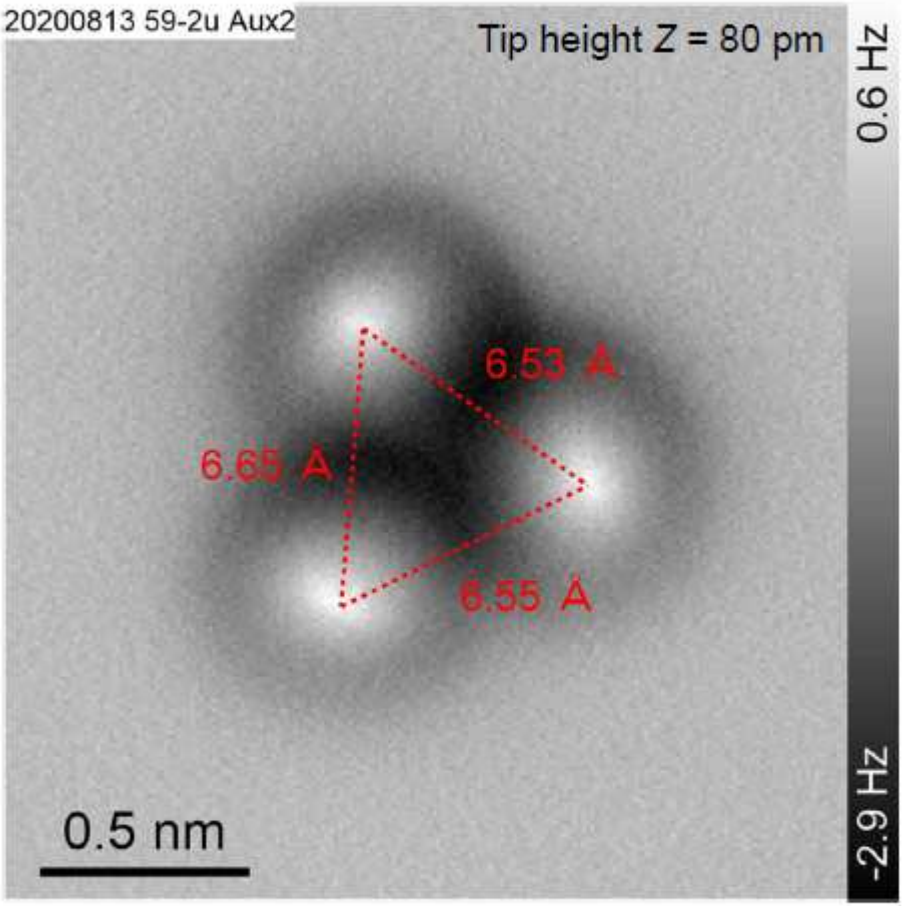
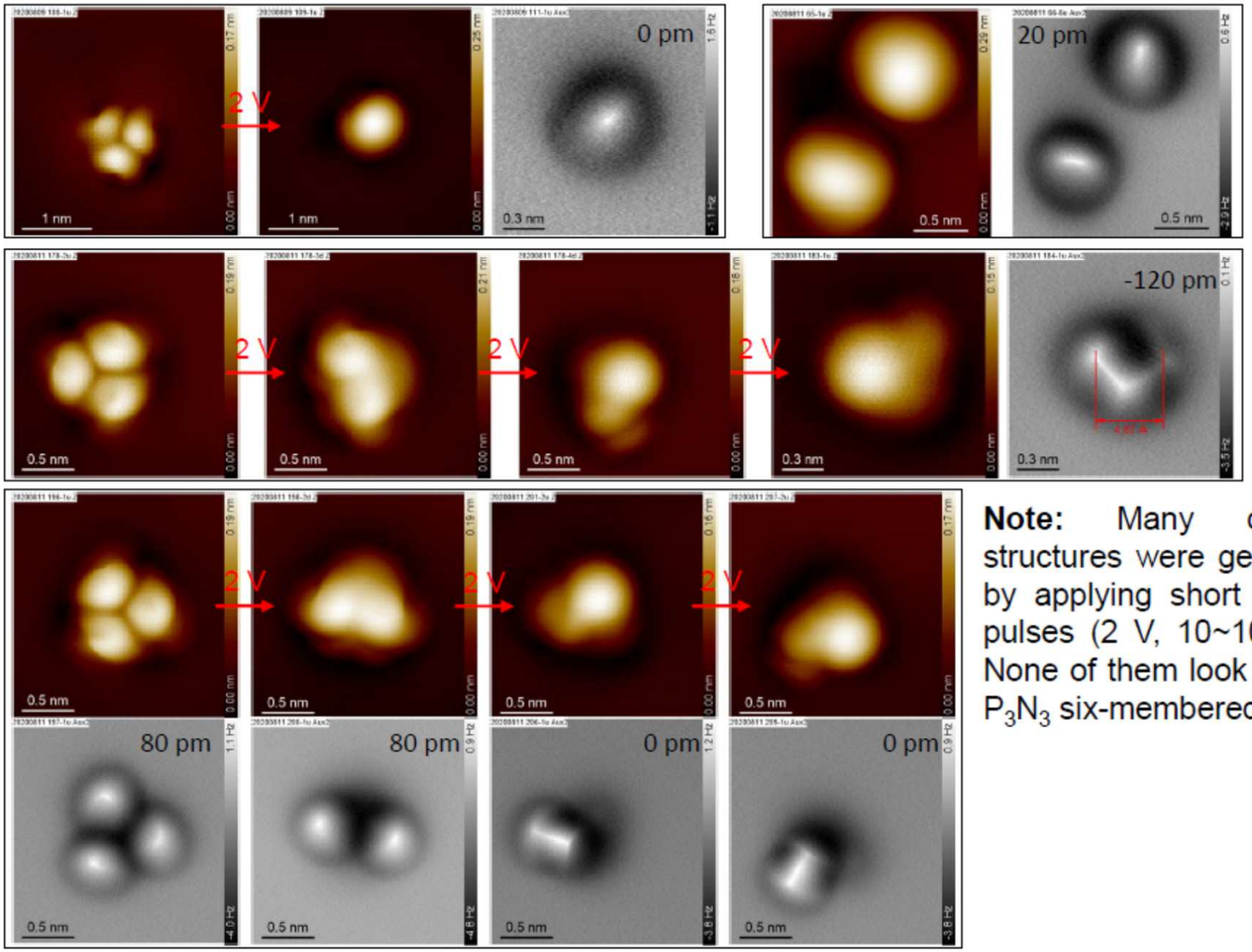
# Quantitative analysis of the AFM images of $P_3N_{21}$






**Note:** The apparent distance between two bright dots in the AFM image is about 6.5 Å. The measured length could be larger than the real distance due to the flexibility of the CO tips used for imaging (Please refer to *Science* **337**, 1326 (2012)).

# Tip-induced reactions of $P_3N_{21}$: More examples

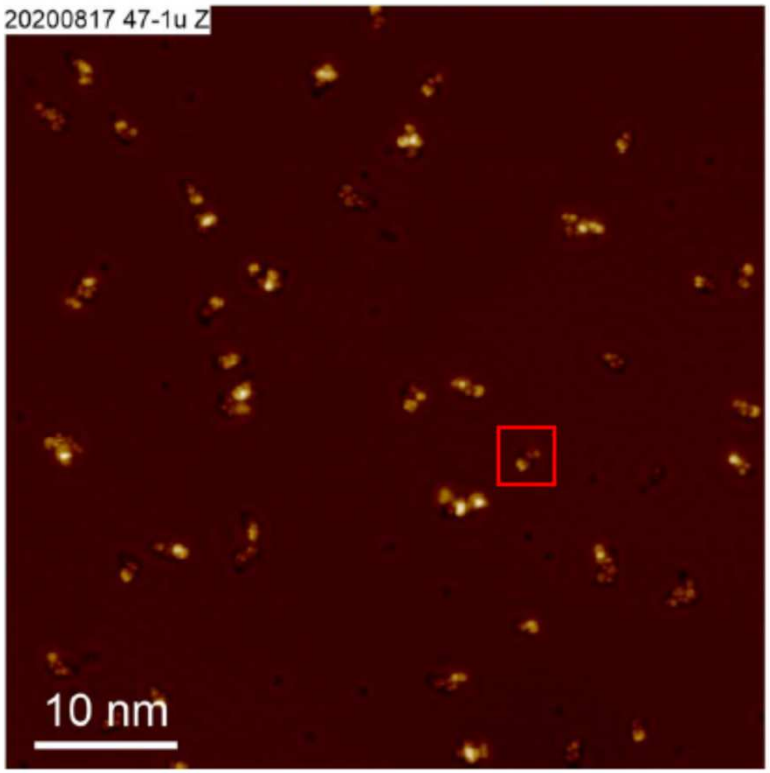


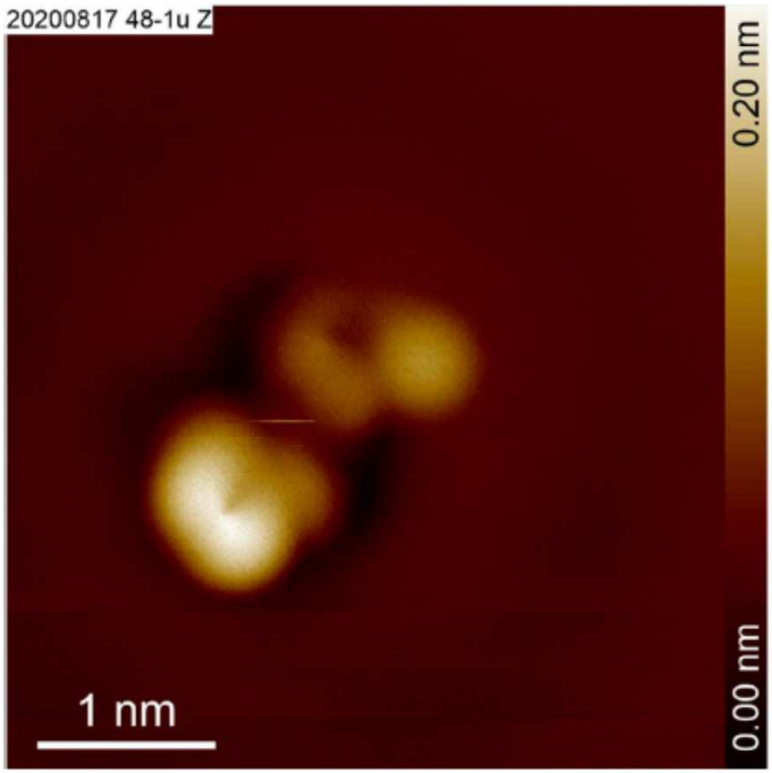

**Note:** Many different structures were generated by applying short voltage pulses (2 V, 10~100 ms). None of them look like the $P_3N_3$ six-membered ring.

# Thermally induced reactions of $P_3N_{21}$ on Cu(111)

$P_3N_{21}$ molecules reacted on Cu(111) at room temperature. Small clusters of molecules formed, making the structure of single molecules elusive.

Annealed the $P_3N_{21}$/Cu(111) sample at RT for 30 min

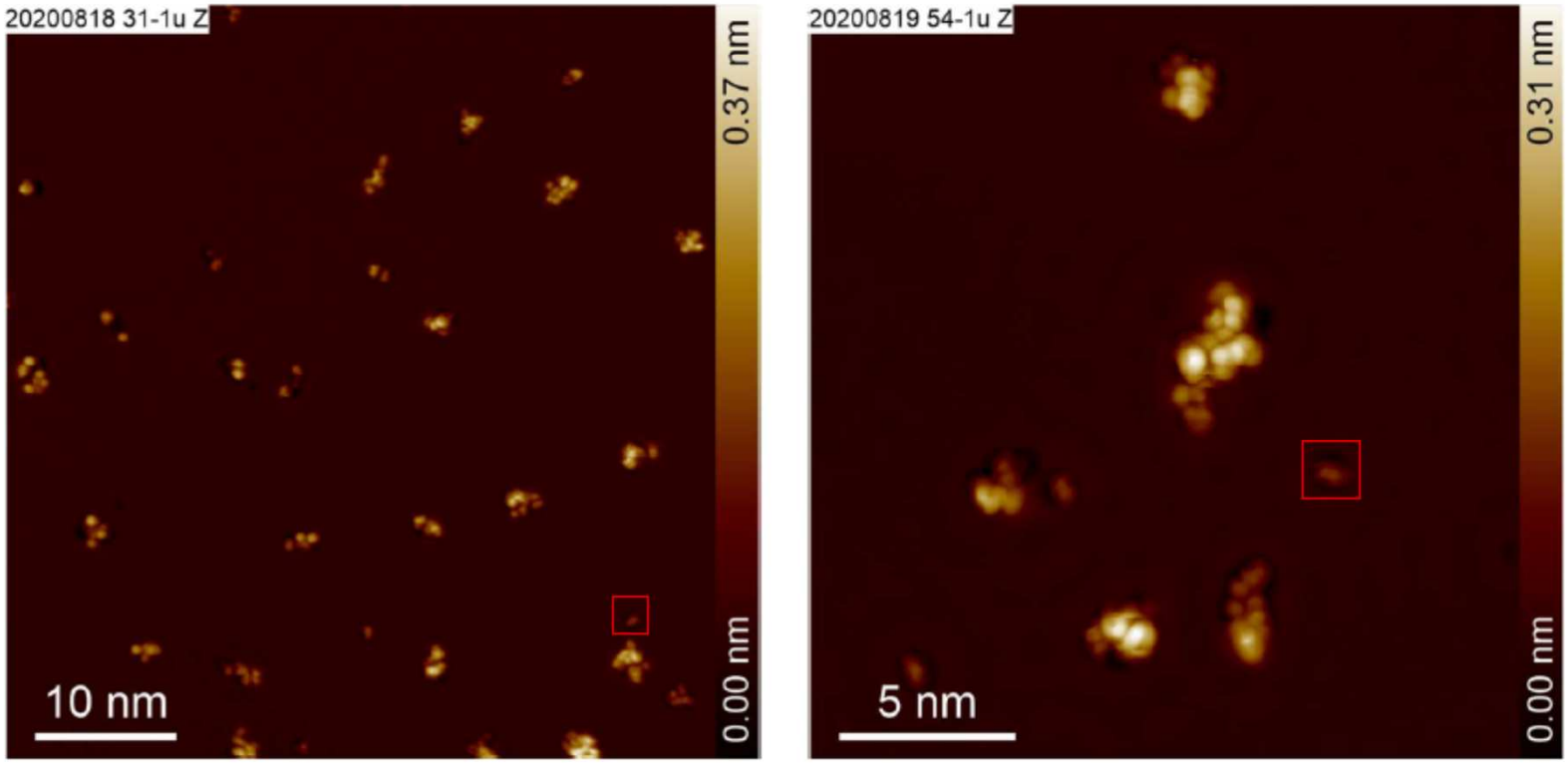


# Thermally induced reactions of $P_3N_{21}$ on Cu(111)

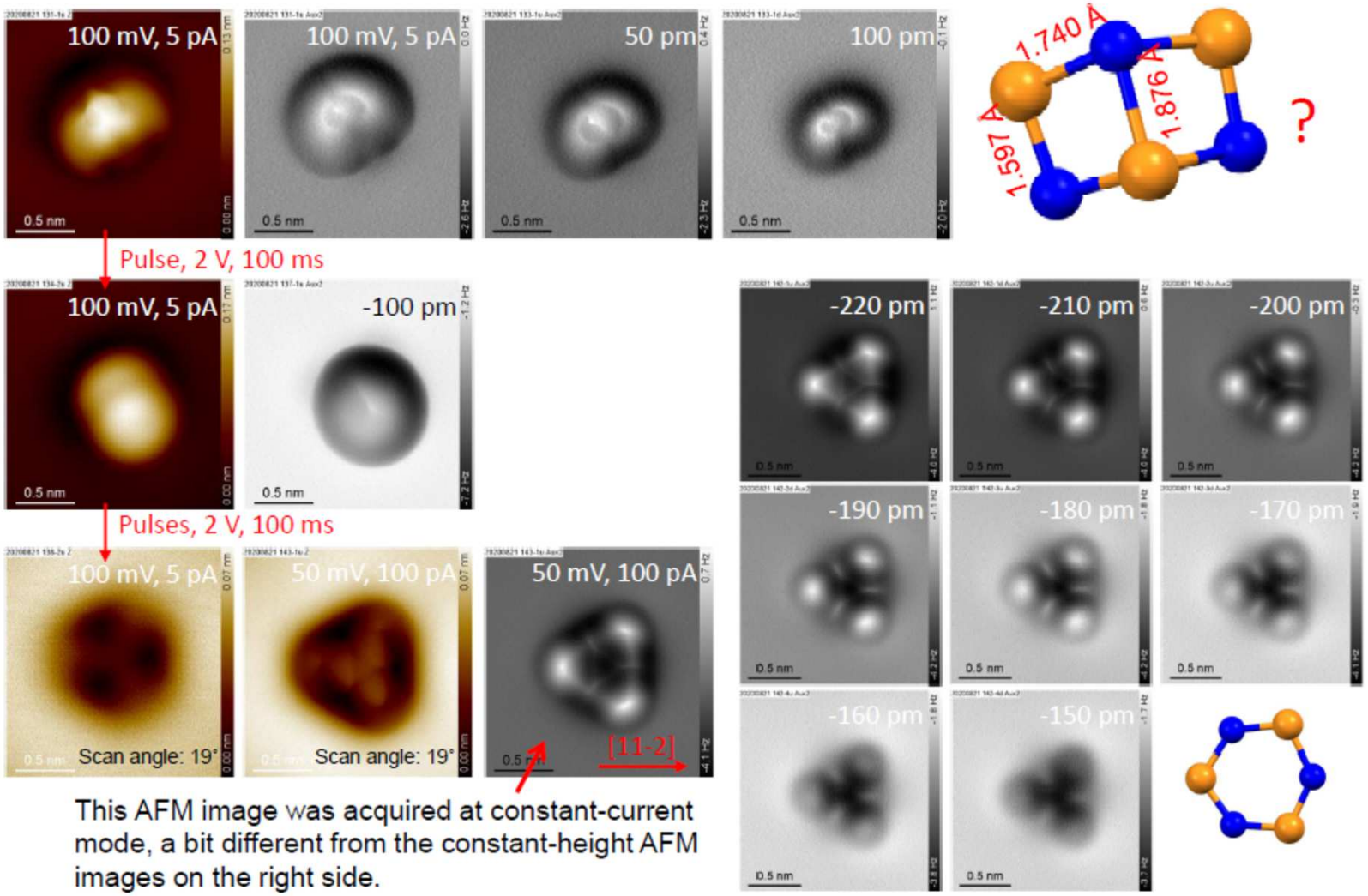
$P_3N_{21}$ molecules further reacted on Cu(111) at 80°C. Small clusters still dominated, while sc single-molecule products were observed.

Annealed the $P_3N_{21}$/Cu(111) sample at 80°C for 30 min



# Imaging and tip-induced isomerization of single molecules

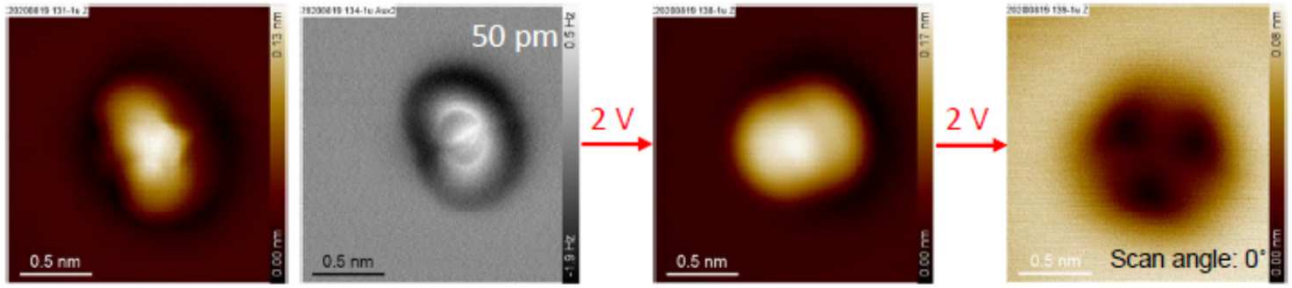
## Molecule 1

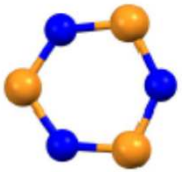


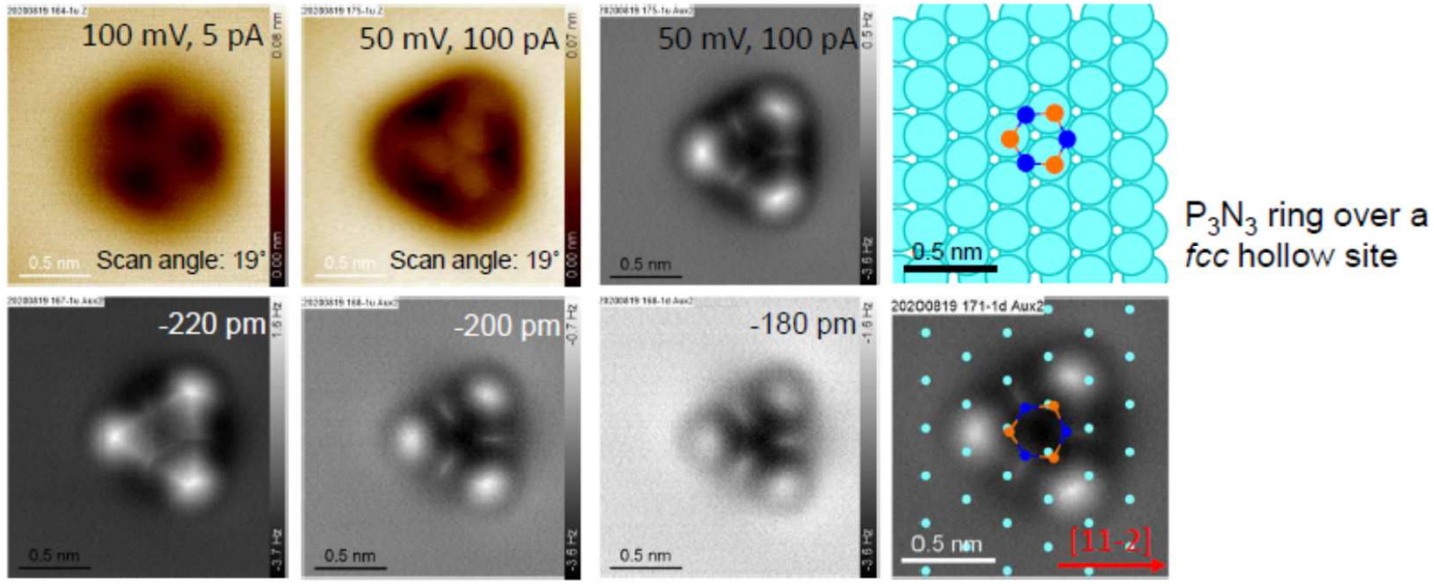

This AFM image was acquired at constant-current mode, a bit different from the constant-height AFM images on the right side.

# Imaging and tip-induced isomerization of single molecules

Molecule 2



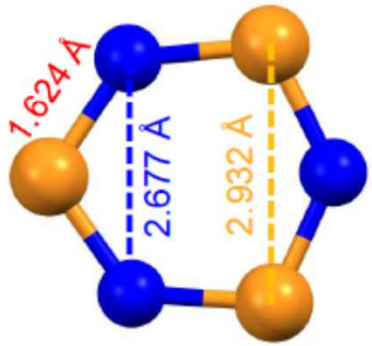





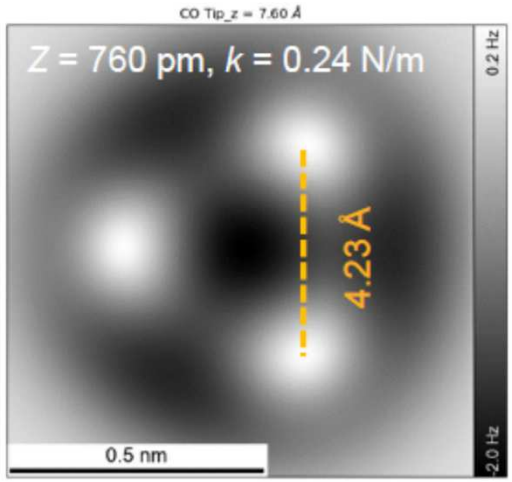

$P_3N_3$ ring over a *fcc* hollow site

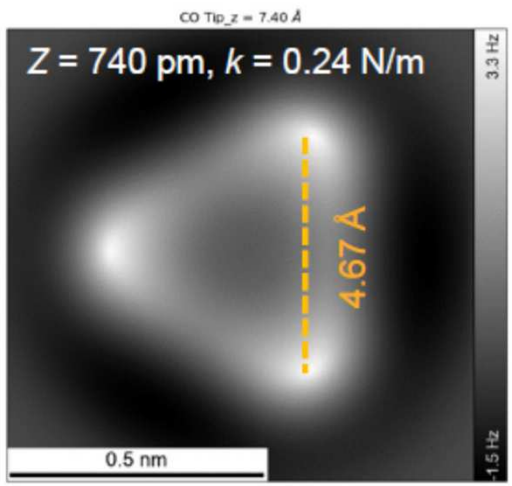
# Size of the $P_3N_3$ ring: Calculation *vs* measurement

Molecular Model

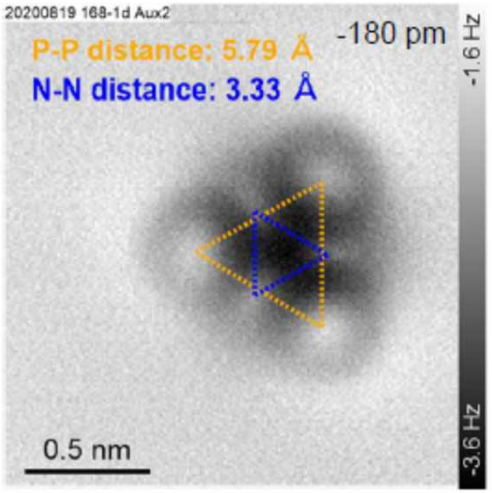


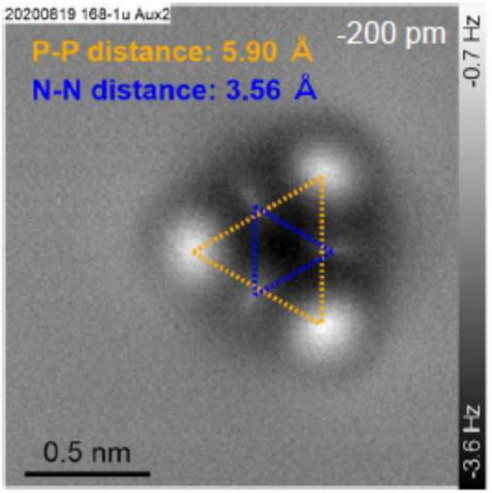

Simulated AFM images




Experimental AFM images




**Note:** In $P_3N_3$ rings, P atoms appear brighter than N atoms, perhaps because of the different atomic radius (P *vs* N = 180 pm *vs* 155 pm).
The bond length is exaggerated due to the flexibility of CO tips. (Please also see slide 34 for more details.)

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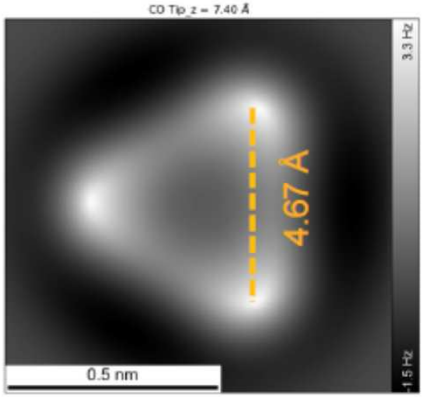
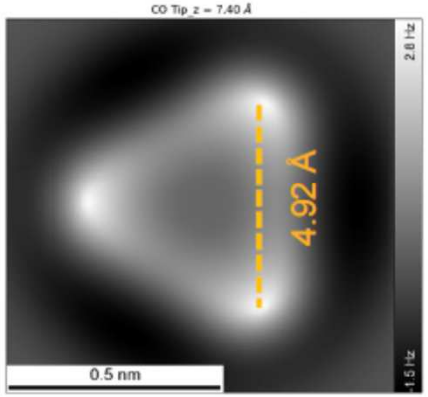
# Distortion of AFM images due to bending of CO tips (Simulation)

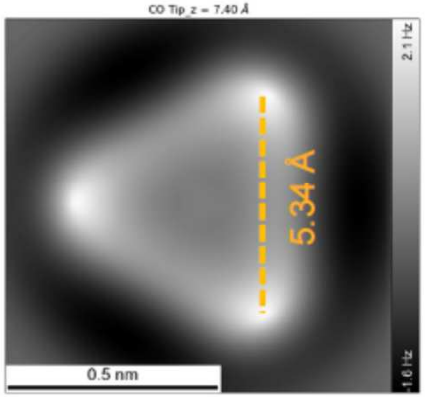
$k$ = 0.24 N/m

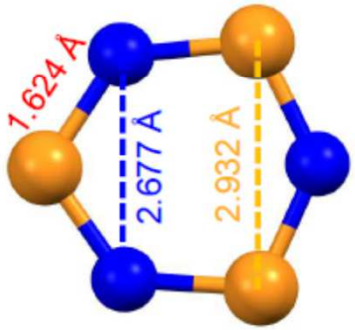



$k$ = 0.20 N/m

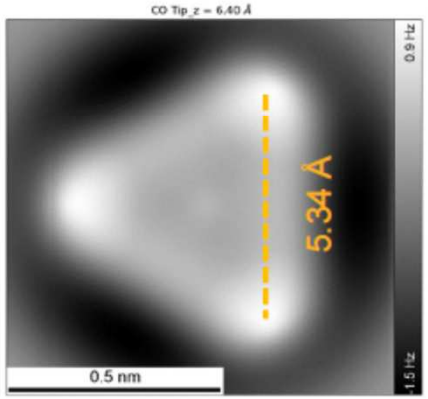



$k$ = 0.15 N/m

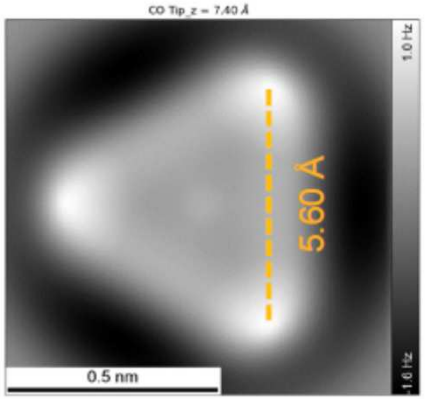



$k$ = 0.10 N/m, r0Probe = 3 Å




$k$ = 0.10 N/m , r0Probe = 4 Å




**Note:** The softer the CO tip is, the larger the distortion will be.

by Dr. Qiqang Zhong

# Acknowledgements

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