μSR Spectroscopy

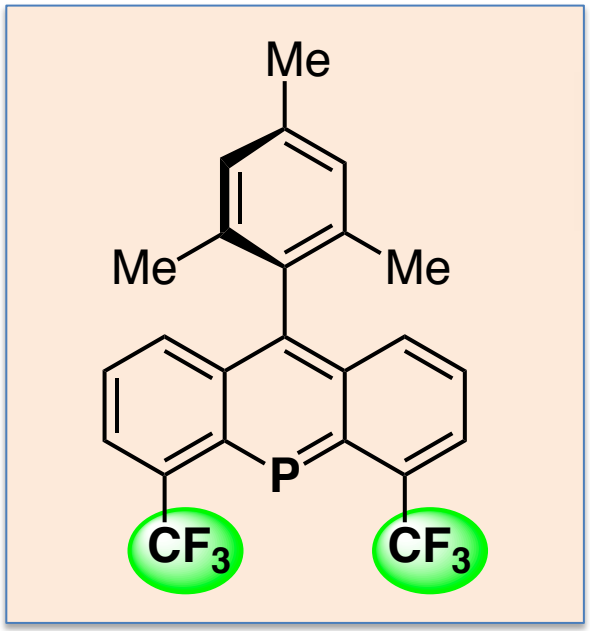
The positive muon (μ^+) is an elementary subatomic particle that is assigned as a member of lepton (spin I = 1/2). High-energy beam of proton from accelerators such as cyclotron and synchrotron produce almost fully polarized muons for analyzing the spin characteristics of materials. The muon has one ninth of the proton mass (0.1126m_p), and the polarized "ultralight proton" is applicable to similar spectroscopic analyses to electron-spin resonance (ESR) and nuclear magnetic resonance (NMR) without the alternative magnetic resonance techniques. The lifetime of muon is 2.2 microseconds, which is useful for monitoring chemical events such as radical addition within 10 ns.

In contact with matter, the positive muon captures an electron and become a muonium (Mu = [μ^+e^-]) that is a light isotope of hydrogen atom. The muoniums have been utilized for monitoring radical reactions of usual unsaturated organic molecules including benzene, alkene, alkyne, and ketone, and the corresponding radicals via muonium addition can be characterized by muon spin rotation/resonance/relaxation (μSR) spectroscopy based on observation of the positrons from the collapsed (polarized) muons.

This paper shows a μSR study on a peri-trifluoromethylated 9-phosphaanthracene which indicated an unprecedented muon isotope effect affording a meta-stable paramagnetic phosphorus heterocycle.

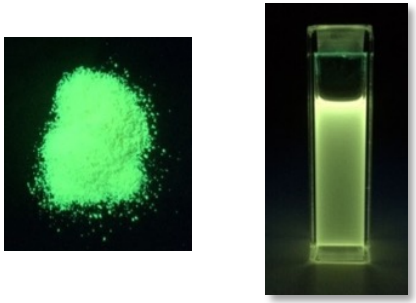
Angew. Chem. Int. Ed. **2021**, *60*, 24034. (Hot Paper)

μSR of CF_3-Phosphaanthracene

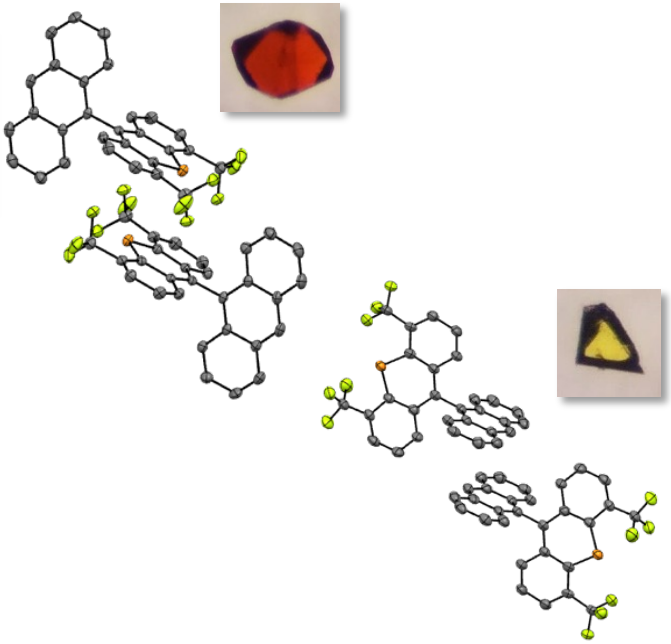


Chem. Asian J. **2018**, *13*, 830.

Air-Tolerant

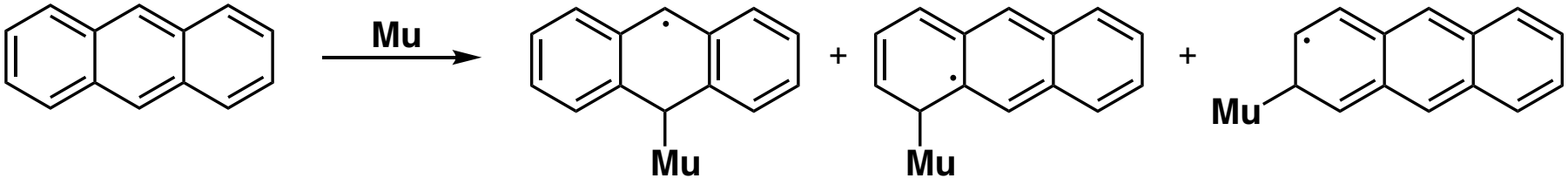


Fluorescence



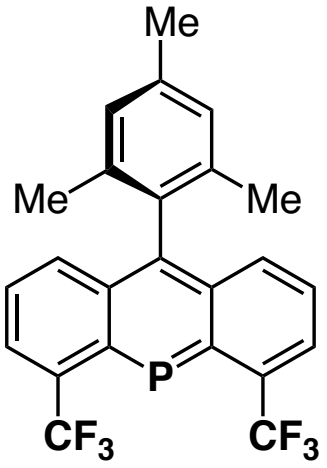
Crystalline Polymorphs

Muonium addition to anthracene

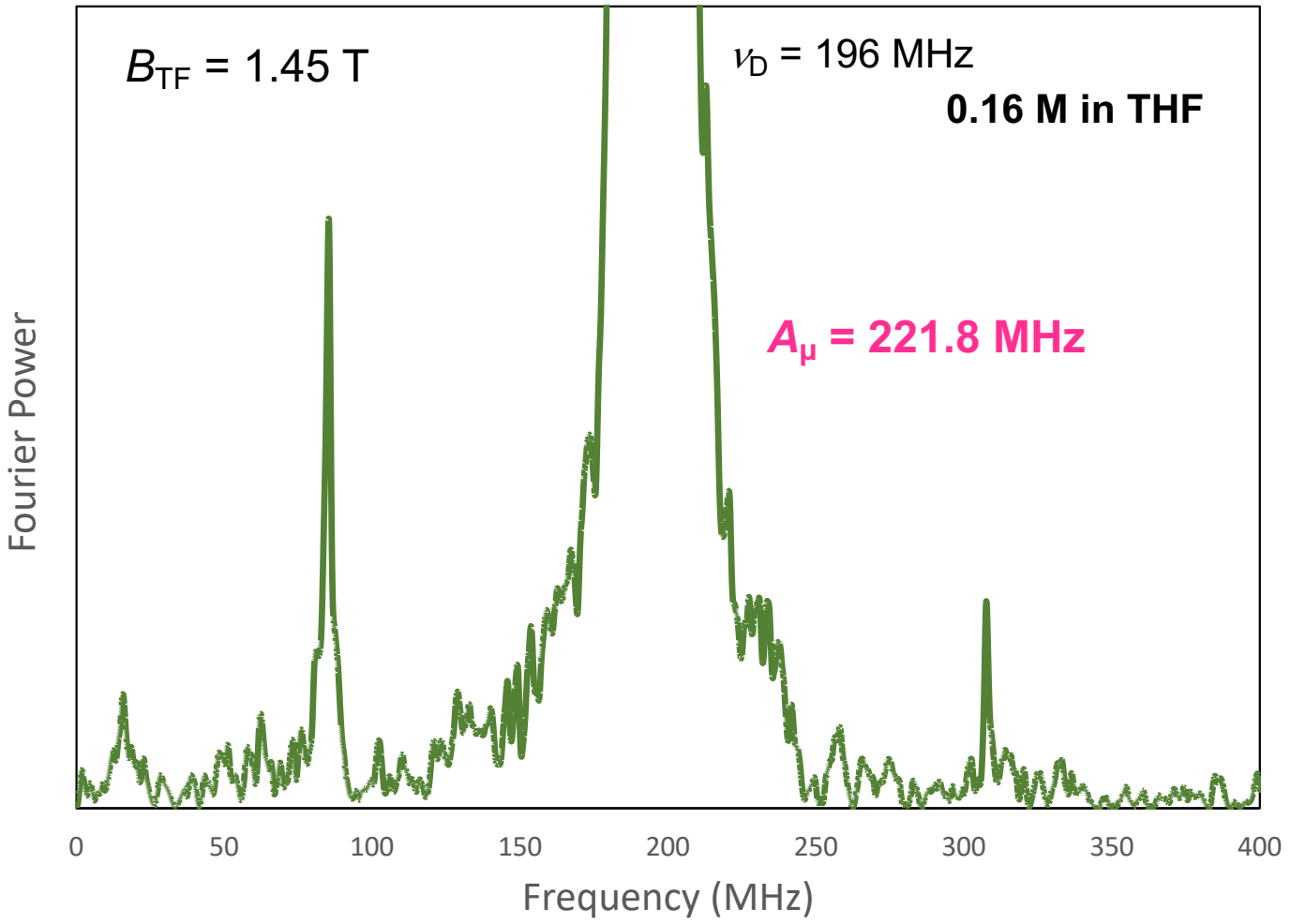


R. M. Macrae, I. D. Reid, J.-U. von Schütz, K. Nagamine, *Physica B* **2000**, *289-290*, 616.

TF-μSR of CF_3-Phosphaanthracene

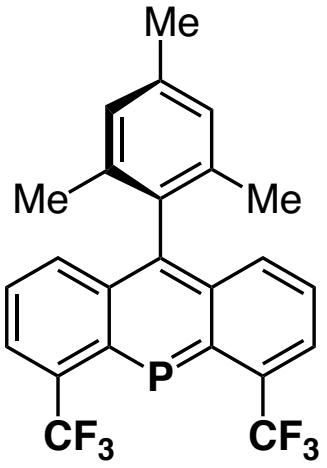


Helios @M15

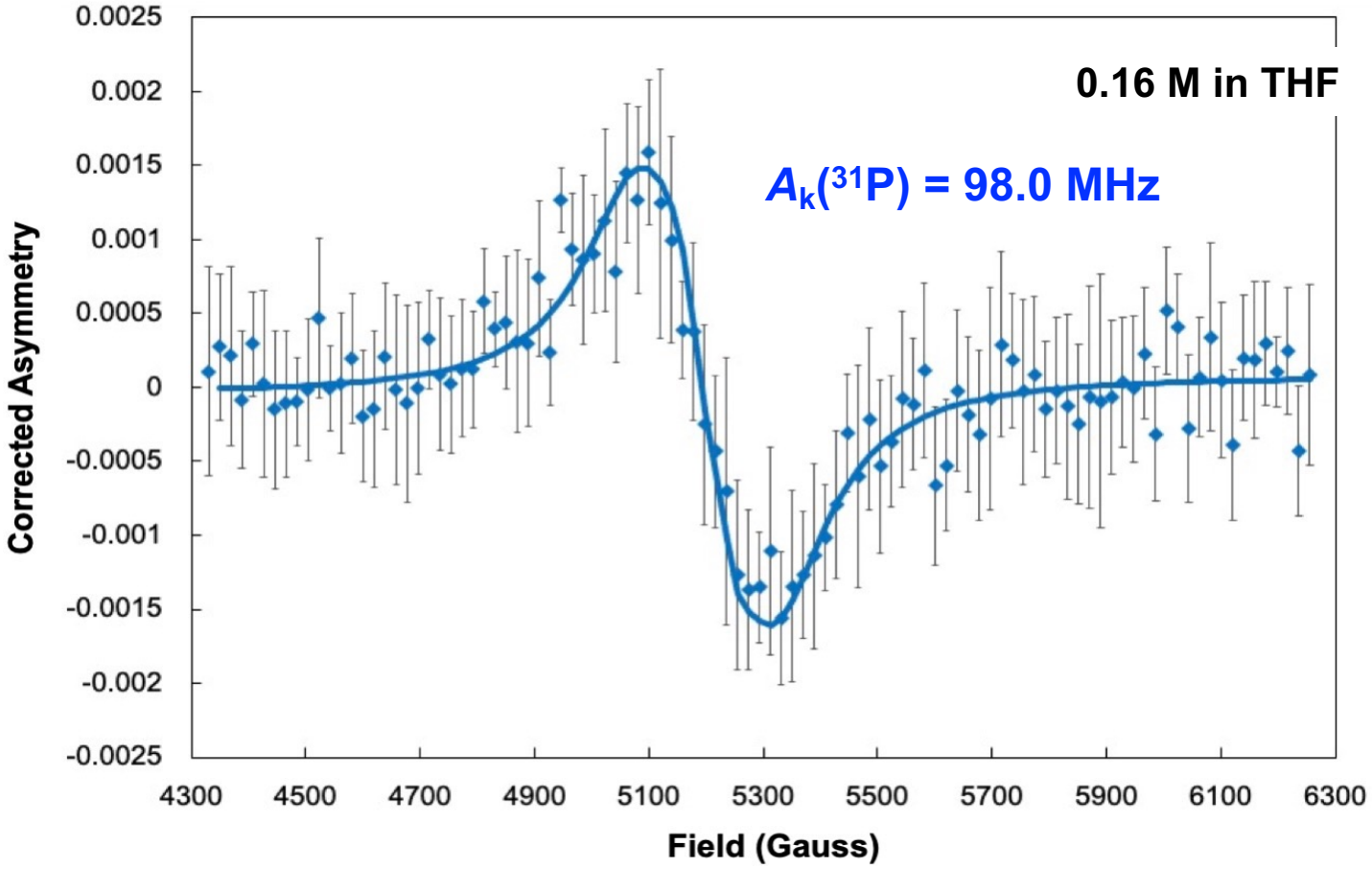


- Regioselective addition affording single paramagnetic species.
- Mu avoids Mes aromatic ring *almost completely*.

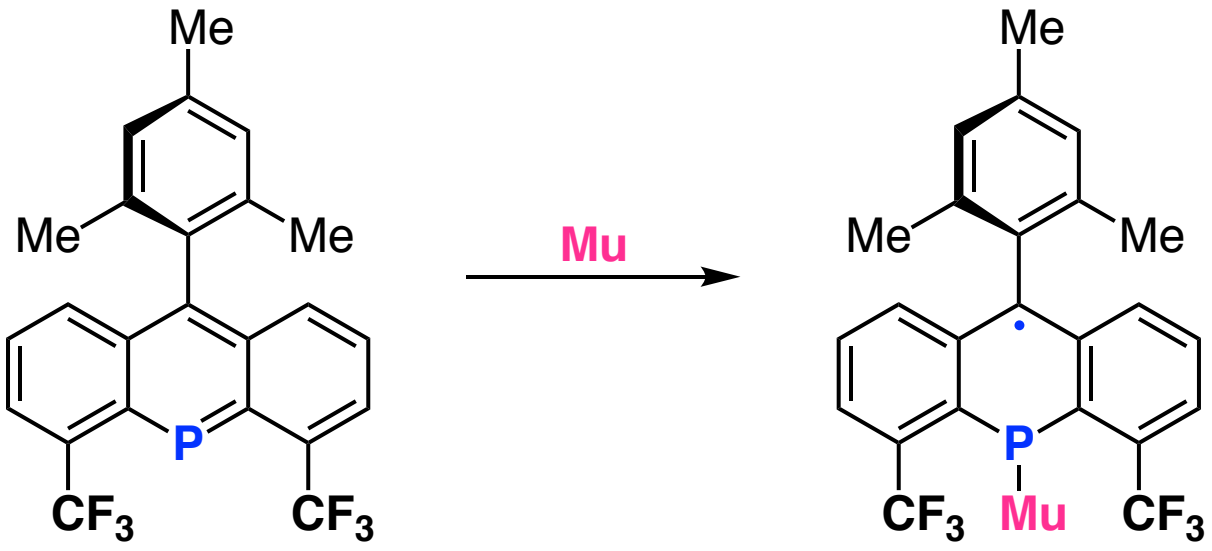
μLCR of CF_3-Phosphaanthracene



Helios @M15



- Regioselective addition affording single paramagnetic species.
- The LCR signal correlates hyperfine interaction of ^{31}P nucleus.



A_μ = 221.8 MHz

$A_k(^{31}P)$ = 98.0 MHz

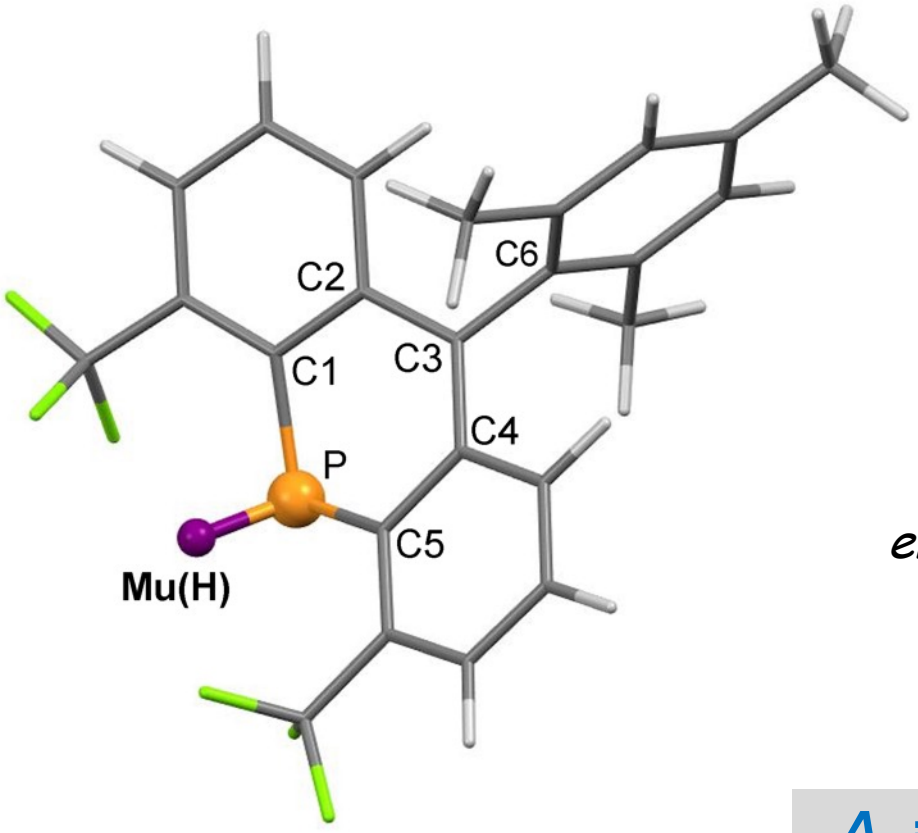
Structure?

Regioselective addition of muonium to the 9-phosphaanthracene was confirmed by the TF-μSR and μLCR spectra. Characterizing the structural parameters by DFT calculations was the subsequent task···

DFT Study for the Muonium Radical

Optimized Structure: No!

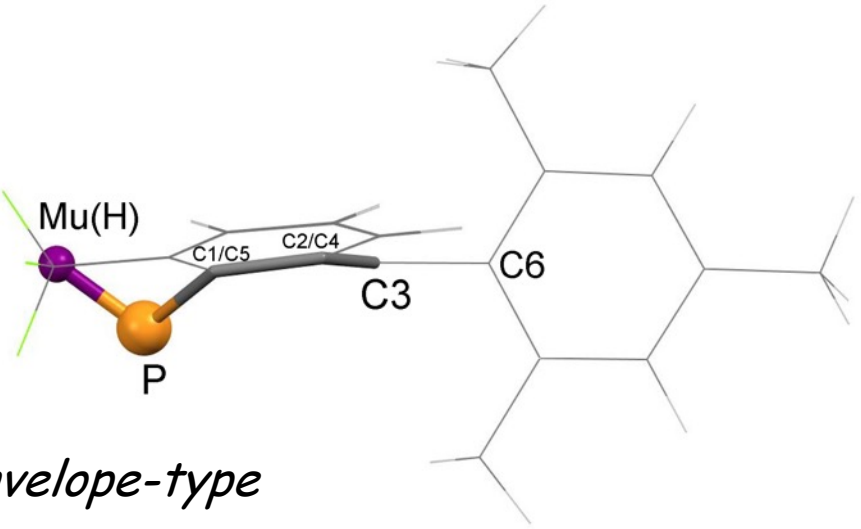
Top view



P–Mu(H) 1.407 Å
P–C1/C5 1.829 Å
C1–C2/C4–C5 1.418 Å
C2–C3/C3–C4 1.442 Å

UωB97XD/6-311G(d,p)

Side view



envelope-type

C6–C3···P 163.8°
C3···P–Mu 127.9°

Experimental

A_μ = 221.8 MHz

$A_k(^{31}P)$ = 98.0 MHz

A_μ = 106.8 MHz

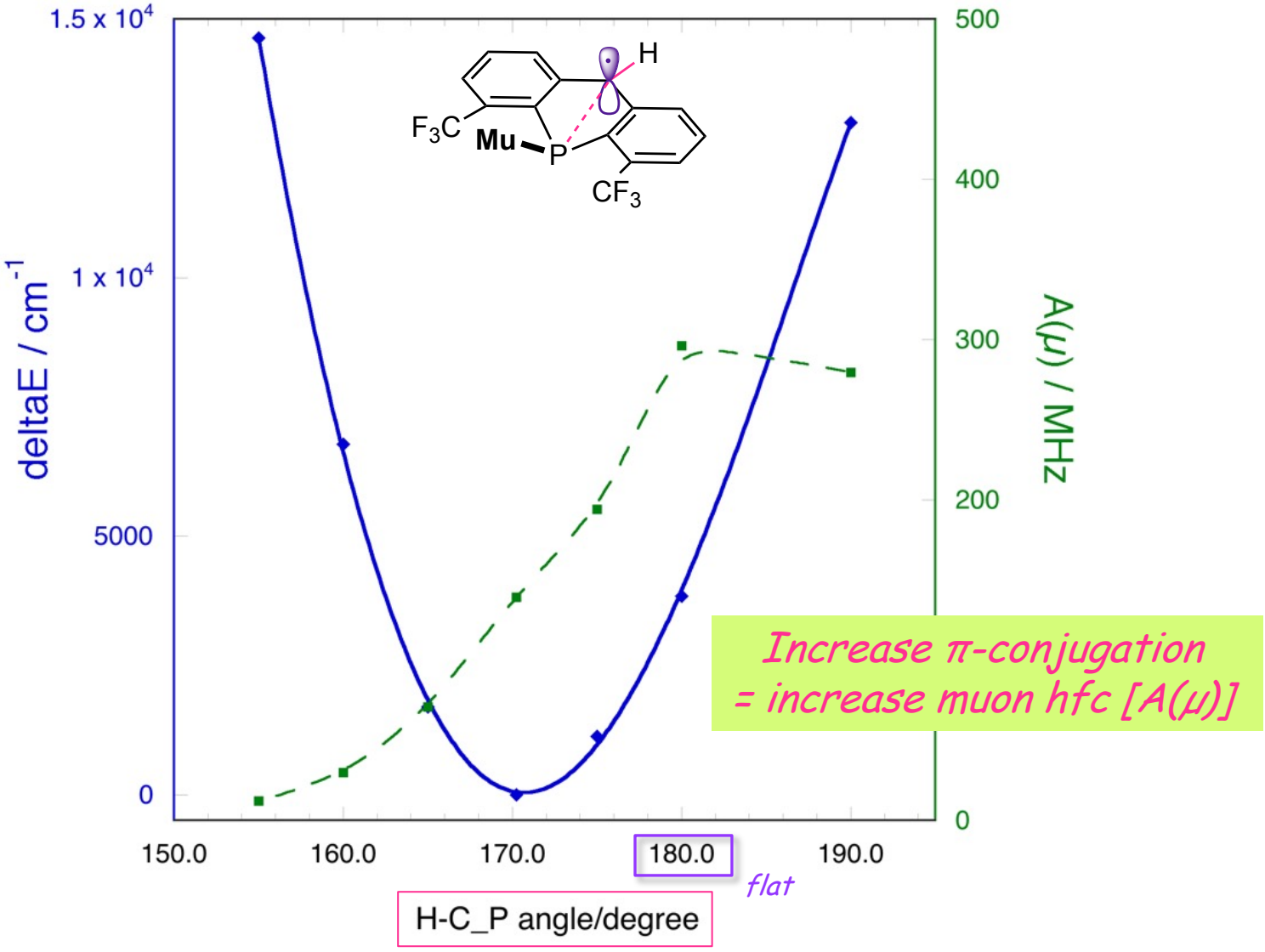
$A_k(^{31}P)$ = 111.9 MHz

Mismatched

Large Zero-Point Energy
(Muon Isotope Effect)

Muon Isotope Effect: *Vibrational Averaging*

Ring flattening = *Unprecedented isotope effect*

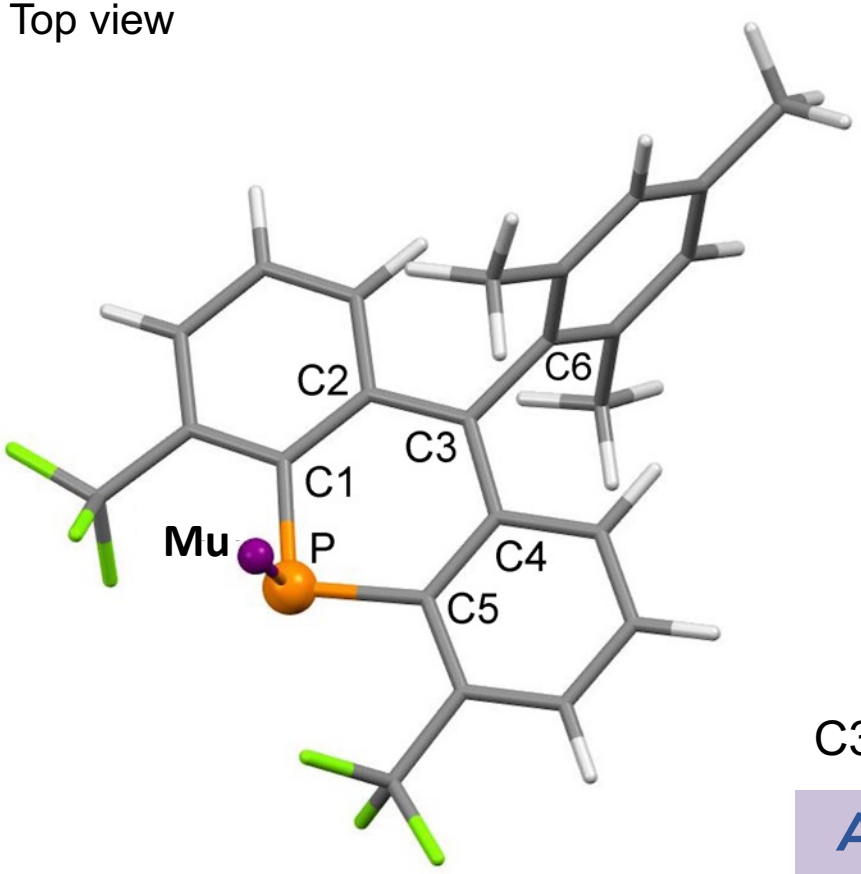


UωB97XD/6-311G(d,p)

DFT Study for the Muonium Radical

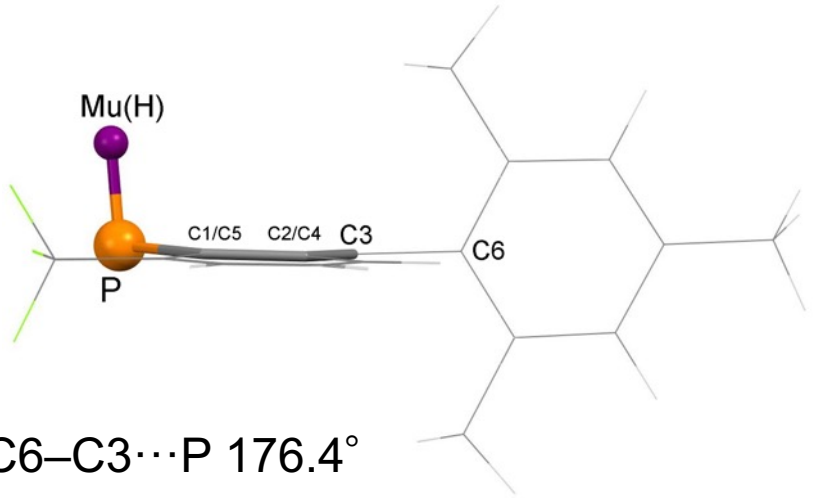
Quasi-Stable Structure: Yes!

Top view



P–Mu(H) 1.416 Å
P–C1/C5 1.837 Å
C1–C2/C4–C5 1.418 Å
C2–C3/C3–C4 1.442 Å

Side view



C6–C3···P 176.4°

C3···P–Mu 97.0° (opt)

A_μ = 241.3 MHz
A_P = 74.4 MHz

modify

C3···P–Mu 102.0°

A_μ = 241.8 MHz
A_P = 96.4 MHz

Experimental

A_μ = 221.8 MHz
$A_k(^{31}P)$ = 98.0 MHz

UωB97XD/6-311G(d,p)