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Authors	Shigekazu Ito, Hikaru Akama, Yasuhiro Ueta, Iain McKenzie, K.M. Kojima
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Muonium Addition to the Radicalic Carbon in 1,3-Diphosphacyclobutane-2,4-diyl[#]

Shigekazu Ito,*[1] **Hikaru Akama,**[1]
Yasuhiro Ueta,[1] **Iain McKenzie,**[2]
and Kenji M. Kojima[2]

S. Ito

[1]Department of Applied Chemistry, School
of Materials and Chemical Technology,
Tokyo Institute of Technology, 2-12-1-H113,
Ookayama, Meguro-ku, Tokyo 152-8552, Japan

[2]Centre for Molecular and Materials Science, TRIUMF,
4004 Wesbrook Mall, Vancouver, BC, V6T 2A3, Canada

E-mail: ito.s.ao@m.titech.ac.jp

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Abstract

When a crystalline 1,3-diphosphacyclobutane-2,4-diyl bearing a 3,5-dichloro-2,4,6-triazine substituent was irradiated with muon beam, two paramagnetic species showing muon hyperfine coupling constants (hfcs) of 4.5 MHz and 6.5 MHz were produced via addition of muonium. These observed paramagnetic species are consistent with the *cis* and *trans* isomers of the C-muoniated 1,3-diphosphacyclobutane-2,4-diyl.

Keywords: Radicals | Phosphorus heterocycles | Muon spin spectroscopy

1. Introduction

Cyclobutane-1,3-diyl is the most fundamental cyclic biradical, and is normally quite unstable and observable only under cryogenic conditions.[1,2] However, exchange of the skeletal carbon atoms with other main group elements is a promising approach to synthesize isolable congeners of cyclobutane-1,3-diyl.[3] 1,3-Diphosphacyclobutane-2,4-diyl is a heavier congener of cyclobutane-1,3-diyl bearing radicalic carbon centres, and Niecke and co-workers reported the first isolable derivative.[4] Subsequently, air-tolerant 1,3-diphosphacyclobutane-2,4-diyls have been developed by repositioning the sterically encumbered 2,4,6-tri-*t*-butylphenyl (Mes*) substituents to the position beside the radicalic carbons.[5] The air-tolerant 1,3-diphosphacyclobutane-2,4-diyl system has been useful to synthesize several functional singlet biradical(oid) derivatives by utilizing the sterically encumbered 1,3-diphosphacyclobuten-4-yl anions/radicals.[6–10]

Radical reactions of heavier cyclobutane-1,3-diyl congeners with radical reagents have been attractive, because the chemical properties would correlate with the electronic properties featured by the two interacting electrons. In our previous report, we utilized muon spin rotation/resonance (μSR) spectroscopy for study of an air-tolerant 1,3-diphosphacyclobutane-2,4-diyl **1**.[11] The positive muon (μ^+) of light proton isotope (Mass = 0.1134 amu) for materials research is generated by using a high-energy beam of proton from accelerator facilities via a nuclear reaction affording pi mesons (π^+). The muons obtained in a cyclotron or synchrotron are spin-polarized. The muon decomposition with a lifetime of 2.2 μs provides a positron together with a pair of neutrinos. In contact with most organic substances behaving as insulators or semiconductors, μ^+ can capture an electron (e^-) and become a muonium ($\mathrm{Mu} = [\mu^+e^-]$) that is a light isotope of hydrogen. The light H-isotope can add to the heavier unsaturated molecular units and provide the corresponding transient paramagnetic species.[12–15] Figure 1 displays the first characterized muoniation product of 1,3-diphosphacyclobutane-2,4-diyl. The observed radical **2** indicated addition of muonium not to the skeletal radicalic centre but to the phosphorus atom bearing a *t*-butyl group in **1**. The regioselective muoniation of **1** would be promoted by the possible zwitterionic canonical formula **1′** as well as by kinetic control avoiding the larger activation energy for the C-muoniation process.

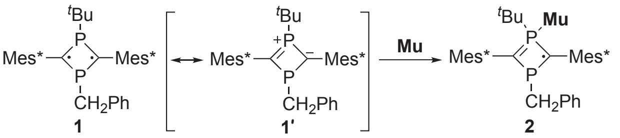

Figure 1. P-Muoniation of 1,3-diphosphacyclobutane-2,4-diyl.

On the other hand, several phosphorus congeners of cyclobutane-1,3-diyl showed radical-type reactions at the skeletal radicalic centres. Amii *et al.* reported potent radical reactivity of 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl by utilizing, for example, trimethyltin hydride, and other radical-type reactions scavenging radical electrons were also characterized.[16] As one of the relevant examples, Schulz and co-workers have developed reversible H_2 storage by utilizing the P-radical centres of diphosphadiazanediyl.[17] Very recently, reaction of a diphosphadiazanediyl with alkyl bromide providing a persistent radical was reported.[18] These examples prompt characterization of possible radical coupling between the hydrogen species and the radicalic centre of 1,3-diphosphacyclobutane-2,4-diyl.

In the course of μSR studies on 1,3-diphosphacyclobutane-2,4-diyl, we employed 2,4-bis(2,4,6-tri-*t*-butylphenyl)-1-*t*-butyl-3-(3,5-dichloro-2,4,6-triazinyl)-1,3-diphosphacyclobutane-2,4-diyl (**3**). The electron-withdrawing dichlorotriazine unit in **3** promotes the reduced *HOMO-LUMO* energetic gap (1.38 eV), probably enabling easier access to the triplet state.[6,8] In this paper, we succeeded in generating novel muonium adducts of 1,3-diphosphacyclobutane-2,4-diyl by using **3**. The considerably small muon hyperfine coupling constants (hfcs, A_μ) strongly suggested direct coupling between the skeletal radicalic centre of 1,3-diphosphacyclobutane-2,4-diyl and muonium. The structures of the novel paramagnetic species generated by muonium addition to **3** are discussed based on density function theory (DFT) calculations.

2. Experimental

A powder sample of **3** was prepared according to our previous paper,[6] and a pellet of 20 mmϕ × 2 mmT covered with aluminum foil (11 μm thickness) was employed for μSR studies. The muon beamline at the TRIUMF cyclotron (M20 beamline) was used, and the LAMPF spectrometer was employed. In this study, we conducted transverse-field muon spin rotation (TF-μSR) measurements (see Supporting Information and our previous papers[19,20]). Gaussian 09 and ADF2021 software packages were employed for density-functional theory (DFT) calculations.[21,22]

3. Results and Discussion

The TF-μSR spectrum collected at 298 K in a transverse magnetic field (B_{TF}) of 2 kG was analyzed by using musrfit[23] as displayed in Figure 2a. Muoniated radicals are characterized by a characteristic pair of precession frequencies, equally spaced about the diamagnetic signal of $\nu_{\mathrm{D}} = 27.2$ MHz in this case [gyromagnetic ratio of the muon (γ_μ) is $(2\pi) \times 13.553$ KHz/G]. Consequently, the difference between the radical precession frequencies is equal to the muon hfcs (A_μ). As displayed in Figure 2b (enlarged), two radical species can be characterized. The larger muon hfc, $A_\mu{}^{\mathrm{a}}$, of 6.5 MHz is obtained by ν_{R2a} and ν_{R1a}, and similarly the smaller $A_\mu{}^{\mathrm{b}}$ of 4.5 MHz can be determined from ν_{R2b} and ν_{R1b}. These muon hfc parameters $A_\mu{}^{\mathrm{a}}$ and $A_\mu{}^{\mathrm{b}}$ determined by the TF-μSR measurement of **3** are remarkably smaller compared with **2** (46.2 MHz), indicating that muonium avoids interacting with the *t*-butylated phosphorus atom in **3**. In addition, the experimentally determined $A_\mu{}^{\mathrm{a}}$ and $A_\mu{}^{\mathrm{b}}$ parameters indicate that the aryl units in **3** do not capture muonium (*vide infra*). Therefore, it was plausible that muonium added to the radicalic skeletal carbon atoms in **3** affording paramagnetic **4** as a mixture of *trans* and *cis* isomers (Figure 3). Each isomer should be a racemic mixture. Figure S1 shows the TF-μSR spectrum of **3** under $B_{\mathrm{TF}} = 3$ kG ($\nu_{\mathrm{D}} = 40.8$ MHz) transverse field confirming the same muonium adducts as of Figure 2.

To confirm the muoniation process of **3** affording *trans*-**4** and *cis*-**4**, we conducted DFT calculations. The structures were optimized at the UωB97XD/6-311G(d,p) level,[24] and the muon hfcs were estimated by using the UPBE-MBD@rsSC/TZ2P-J//UωB97XD/6-311G(d,p) condition.[25] Figure 4 shows optimized structures of *trans*-**4** (*R* enantiomer) and *cis*-**4** (*S* enantiomer). Both structures of *trans*-**4** and *cis*-**4** show weak distortion of a four-membered phosphorus heterocyclic plane into butterfly-type structure. The skeletal P–C(Mu) distances are considerably long (1.871–1.895 Å), whereas the P–C(rad) lengths are 1.80 Å. Table 1 displays that the absolute muon hfcs of *trans*-**4** and *cis*-**4** are 9.1 MHz and 6.2 MHz, respectively. Almost no deviation of muon hfcs was characterized even by elongation of the C–Mu(H) distances due to the possible light isotope effect.[12b,26] The smaller muon hfc of *cis*-**4** indicates smaller overlap between the P–Mu bonding and the radicalic p-orbital due to the steric effects. The experimentally characterized small $A_\mu{}^{\mathrm{a}}$ and $A_\mu{}^{\mathrm{b}}$ by TF-μSR confirmed that muonium addition to the Mes* aromatic ring in **3** affording muon hfc of ca. 480 MHz is completely avoided. Preliminary DFT calculations for unstable N-muoniated 1,3,5-triazines showed muon hfc of ca. 60 MHz, indicating no muonium addition to the triazine unit in **3**. Muoniation processes toward the skeletal phosphorus atoms in **3** were also examined by DFT calculations, and the optimized structures of **5** and **6** (Figure 5) showed absolute muon hfcs of 35.2 MHz and 9.5 MHz, respectively (Table 1). One of the P-muoniation products **6** showed similar muon hyperfine parameter to *trans*-**4**. However, the relative total energy is considerably high even compared with **5** which is a variant of **2**, probably because the electron-deficient N-heteroaryl substituent destabilizes the positively charged $\lambda^5\sigma^4$ phosphorus

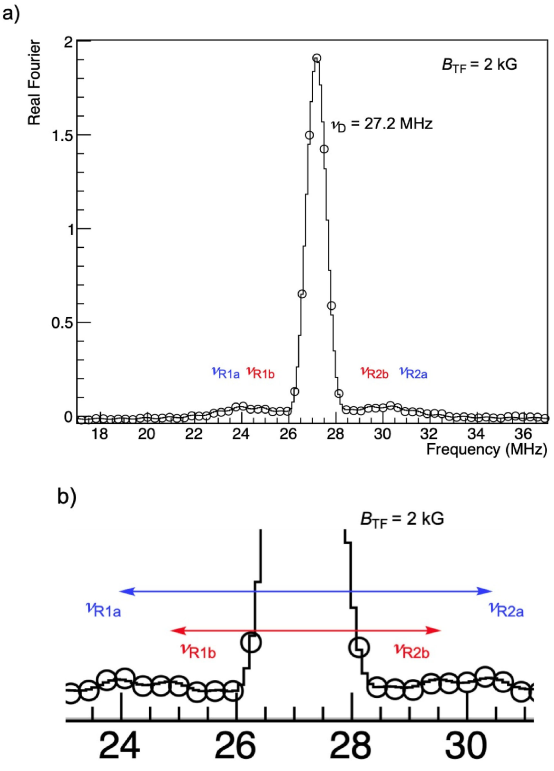

Figure 2. a) TF-μSR spectrum from a powder sample of **3** at 298 K and $B_{\mathrm{TF}} = 2$ kG. A strong diamagnetic resonance of muon (ν_{D}) appears at 27.2 MHz. b) Enlarged TF-μSR spectrum showing two muon hfcs [$A_\mu{}^{\mathrm{a}} = 6.5$ MHz (blue) and $A_\mu{}^{\mathrm{b}} = 4.5$ MHz (red)].

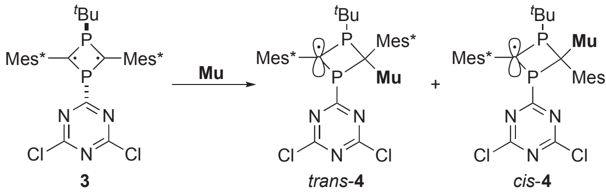

Figure 3. Muonium addition to the skeletal radicalic centres of **3** affording two geometrical isomers *trans*-**4** and *cis*-**4**.

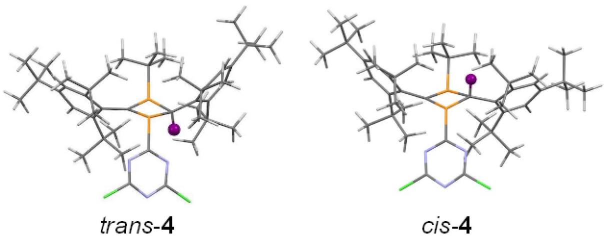

Figure 4. Optimized structures of *trans*-**4** (*R* enantiomer) and *cis*-**4** (*S* enantiomer) at the UωB97XD/6-311G(d,p) level. The muoniums, calculated as the H atoms, are shown as purple balls.

Table 1. DFT calculation results of **4**–**6**

	trans-**4**	*cis*-**4**	**5**	**6**
E_{rel}[a] /kcal mol^{-1}	0.0	+1.9	+22.9	+30.6
muon hfc[b] /MHz	9.1	6.2	35.2	9.5

[a] UωB97XD/6-311G(d,p). [b] UPBE-MBD@rsSC/TZ2P-J//UωB97XD/6-311G(d,p). Absolute value. The muon hfcs are calculated by considering the $\gamma_\mu/\gamma_{\mathrm{p}}$ ratio (3.1833), where γ_{p} is the gyromagnetic ratio of the proton.

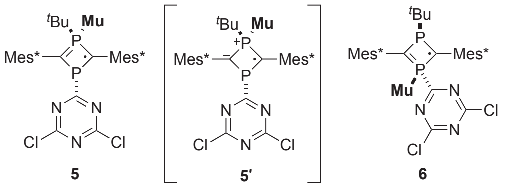

Figure 5. P-Muoniation products of **3**.

unit. Also, the canonical formula **5′** indicates reduction of the negative charge of the ylidic carbon atom, which might destabilize the $\lambda^5\sigma^4$ phosphorus unit by the excessive positive charge. Furthermore, when the isotope effect causing P–Mu(H) bond-elongation of 4% is considered,[11] the increased muon hfc parameter of 14.6 MHz is predicted. Therefore, we conclude that formation of **6** is unlikely.

The novel regioselective addition of muonium to the 1,3-diphosphacyclobutane-2,4-diyl unit might correlate with possible contribution of the triplet state of **3**. In the triplet state, the skeletal C–P distances are elongated compared with the singlet state,[4,27] and access of muonium to the skeletal carbon might be easier compared with the muoniation of the singlet state that can promote the P-selective muoniation affording **2**.[11] Although more detailed studies are required, the reduced singlet-triplet energetic difference of 1,3-diphosphacyclobutane-2,4-diyl might induce the C-muoniation leading to the thermodynamically favorable paramagnetic P-heterocyclic structure putatively via radical-radical coupling process.

4. Conclusion

We demonstrated μSR studies on the P-triazine-substituted 1,3-diphosphacyclobutane-2,4-diyl **3**. In contrast to our previous μSR of the highly electron-donating derivative **1**, the skeletal radicalic carbon in **3** can capture muonium of light hydrogen surrogate affording the thermodynamically favorable paramagnetic phosphorus heterocycles *trans*-**4** and *cis*-**4**. The straightforward coupling of muonium and the radicalic carbon in **3** indicates the potent comparable biradical character of 1,3-diphosphacyclobutane-2,4-diyl with its carbon congener, cyclobutane-1,3-diyl.

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Supporting Information

Brief description of TF-μSR and DFT calculations. This material is available on https://doi.org/10.1246/bcsj.20210352.

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\# This paper is dedicated to Prof. Masaaki Yoshifuji on the occasion of his 80th birthday.

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