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Muonium Addition to the Radical Carbon in 1,3-Diposphacyclobutane-2,4-diyl#

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Abstract

When a crystalline 1,3-diposphacyclobutane-2,4-diyl bearing a 3,5-dichloro-2,4,6-triazine substituent was irradiated with muon beam, two unsaturated muonic species were observed as muonic species showing muon hyperfine coupling constants (hfc's) 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-μ1,3-diposphacyclobutane-2,4-diyl.

Keywords: Radicals | Phosphorus heterocycles | Muon spin spectroscopy

1. Introduction

Cyclobutane-1,3-diy1 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 stable congeners of cyclobutane-1,3-diy1.3 1,3-Diposphacyclobutane-2,4-diyl is a heavier congener of cyclobutane-1,3-diy1 bearing radical carbon centres, and Niecke and co-workers reported the first isomeric derivative.4 Subsequently, air-tolerant 1,3-diposphacyclobutane-2,4-diyls have been developed by repositioning the sterically encumbered 2,4,6-tri-i-butylphenyl (Mes)3 substituents to the position beside the radicalic carbons.5 The air-tolerant 1,3-diposphacyclobutane-2,4-diyl system has been useful to synthesize several functional singlet biradicaloid derivatives by utilizing the sterically encumbered 1,3-diposphacyclobutene-4-y1 anions/derivatives.6-10

Radical reactions of heavier cyclobutane-1,3-diy1 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-diposphacyclobutane-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 π 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 (Mu = [μ+ 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 muonium product of 1,3-diposphacyclobutane-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 muonation 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-muonium process.

On the other hand, several phosphorus congeners of cyclobutane-1,3-diy1 showed radical-type reactions at the skeletal radicalic centres. Amii et al. reported potent radical reactivity of 1,3-dihalora-2,4-diposphonocyclobutane-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 H2 storage by utilizing the P-radicale centre of diposphadiazanediyl.17 Very recently, reaction of a diposphadiazanediyl 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-diposphacyclobutane-2,4-diyl.

In the course of μSR studies on 1,3-diposphacyclobutane-2,4-diyl, we employed 2,4-bis[2,4,6-tri-i-butylphenyl]-1-i-butyl-3-(3,5-dichloro-2,4,6-triazinyl)-1,3-diposphacyclobutane-2,4-diyl (3). The electron-withdrawing dichlorotrizine unit in 3 promotes the reduced HOMOLUMO 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-diposphacyclobutane-2,4-diyl by using 3. The considerably small muon hyperfine coupling constants (hfcs, Aμ) strongly suggested direct coupling between the skeletal radicalic centre of 1,3-diposphacyclobutane-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,9 and a pellet of 20 mmol x 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 papers9,20). Gaussian 09 and ADF2021 software packages were employed for density-functional theory (DFT) calculations.21,22

![Figure 1. P-Muoniation of 1,3-diposphacyclobutane-2,4-diyl.](image-url)
3. Results and Discussion

The TF-μSR spectrum collected at 298 K in a transverse magnetic field \(B_{TF}\) of 2 kG was analyzed using musfrit\(^{23}\) as displayed in Figure 2a. Muoniated radicals are characterized by a characteristic pair of precession frequencies, equally spaced about the diamagnetic signal of \(\nu_{D} = 27.2\) MHz in this case [gyromagnetic ratio of the muon \(\gamma_{\mu}\) is \((2\pi) \times 13.553\) KHz/G]. Consequently, the difference between the radical precession frequencies is equal to the muon hfc \(A_{\mu}\). As displayed in Figure 2b (enlarged), two radical species can be characterized. The larger muon hfc, \(A_{\mu}^{a}\), of 6.5 MHz is obtained by \(\nu_{R2a}\) and \(\nu_{R1a}\) and similarly the smaller \(A_{\mu}^{b}\) of 4.5 MHz can be determined from \(\nu_{R2b}\) and \(\nu_{R1b}\). These muon hfc parameters \(A_{\mu}^{a}\) and \(A_{\mu}^{b}\) 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 \(A_{\mu}^{a}\) and \(A_{\mu}^{b}\) 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 \(B_{TF} = 3\) kG \((\nu_{D} = 40.8\) 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 UoB97XD/6-311G(d,p) level,\(^{26}\) and the muon hfc were estimated by using the UPBE-MBD@rsSC/TZ2P-J//UoB97XD/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 \(A_{\mu}^{a}\) and \(A_{\mu}^{b}\) 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. Muonium 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 \(\beta\)-π\(^a\) phosphorus.

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

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<th>trans-4</th>
<th>cis-4</th>
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<th>6</th>
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<tr>
<td>(E_{rad})(^{[a]}) /kcal mol(^{-1})</td>
<td>0.0</td>
<td>+1.9</td>
<td>+22.9</td>
<td>+30.6</td>
</tr>
<tr>
<td>muon hfc(^{[b]}) /MHz</td>
<td>9.1</td>
<td>6.2</td>
<td>35.2</td>
<td>9.5</td>
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\(^{[a]}\)UoB97XD/6-311G(d,p). \(^{[b]}\)UPBE-MBD@rsSC/TZ2P-J//UoB97XD/6-311G(d,p). Absolute value. The muon hfc are calculated by considering the \(\gamma_{\mu}/\gamma_{P}\) ratio (3.1833), where \(\gamma_{P}\) is the gyromagnetic ratio of the proton.
unit. Also, the canonical formula 5c indicates reduction of the negative charge of the ylidic carbon atom, which might destabilize the $\lambda^1\sigma$ phosphorus unit by the excessive positive charge. Furthermore, when the isotope effect causing P–Mu(H) bond-elongation of 4% is predicted, 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-diphenylcyclobutane-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, and access of muonium to the skeletal carbon might be easier compared with the muonium of the singlet state that can promote the P-selective muonium affording 2.11 Although more detailed studies are required, the reduced singlet-triplet energetic difference of 1,3-diphenylcyclobutane-2,4-diyl might induce the C-muonium 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-diphenylcyclobutane-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-diphenylcyclobutane-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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