Muonium Adducts of Diacetylenes

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Addition of muonium takes place at the terminus of the conjugated diacetylene unit in $MeC\equiv C{-}C\equiv CMe$ to give $MeC(Mu){=}\dot{C}{-}C\equiv CMe$ radicals, but to the adjacent position in $Me_3SiC\equiv C{-}C\equiv CSiMe_3$ to give $Me_3Si\dot{C}{=}C(Mu){-}C\equiv CSiMe_3$ radicals.

In previous studies,[1,2] we have measured the transverse field (TF) μSR spectra[3] of vinyl radicals formed by the addition of muonium (μ^+e^-) to acetylene derivatives. The key to this work was the use of acetylenes substituted with conjugating substituents such as phenyl and trimethylsilyl which render the radical centre linear (or rigid), otherwise the characteristic inversion of the radical centre in a bent vinyl radical provides an efficient relaxation mechanism which broadens the lines beyond detection. We now report preliminary results that provide an extension of this interesting chemistry to diacetylenes.

The results are quite distinct for $MeC\equiv C{-}C\equiv CMe$ and $Me_3SiC\equiv C{-}C\equiv CSiMe_3$. In the former case, the unique radical that is observed (Fig. 1) has a muon-hyperfine coupling of 394 MHz, which is equivalent to a proton coupling of 44.2 G† (obtained by multiplying by the proton : muon magnetic moment ratio and assuming that $g = 2.0023$). This may be compared with the coupling to the $=CH_2$ protons in the radical $H_2C{=}\dot{C}{-}C\equiv CH$ (43.4 G), formed by hydrogen atom addition to $HC\equiv C{-}C\equiv CH$ in an argon matrix at 4 K.[4] From these data, a hyperfine isotope ratio of 1.02 may be estimated, which is rather low even for radicals that are unable to undergo conformational averaging[5] (when this is possible, higher ratios of *ca.* 1.4 are normal); however, we have shown previously[2] that the reduced muon coupling (47.1 G) in the $Ph\dot{C}{=}C(Mu)H$ radical is greater than that in the $Ph\dot{C}{=}C(Mu)Me$ radical and so we might obtain an 'effective' isotope ratio of 1.08 on the assumption that there is either differential delocalisation involving C–C or C–H bonds in the groups C(Me)Mu or

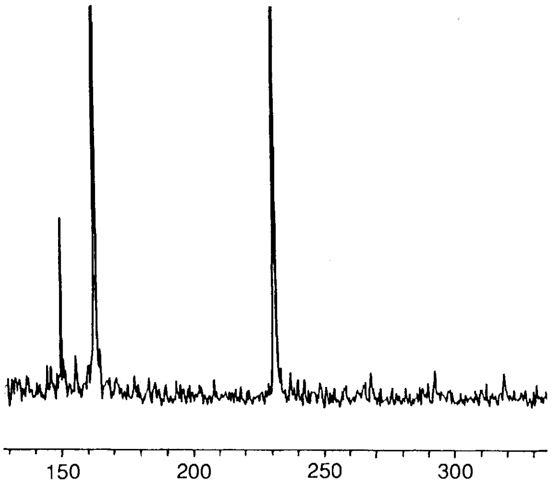

Fig. 1 TF-μSR spectrum assigned to radicals $MeC(Mu){=}\dot{C}{-}C\equiv CMe$

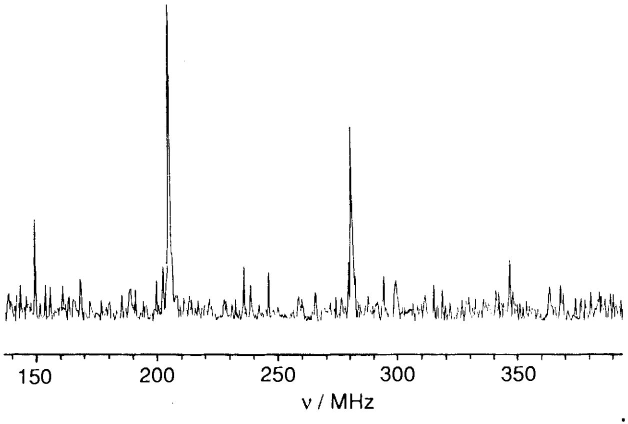

Fig. 2 TF-μSR spectrum assigned to the radical $Me_3Si\dot{C}{=}C(Mu){-}C\equiv CSiMe_3$

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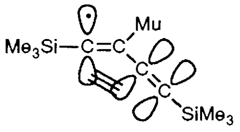
† 1 G = 10^{-4} T.



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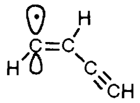

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C(H)Mu, or differential interaction of these groups with the unpaired electron due to their differing energies.

For $\mathrm{Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3}$, a single radical species is again observed, but with a substantially larger coupling of 486 MHz which is equivalent to a proton coupling of 54.5 G. This means that the muonium cannot have added to the terminal carbon atom, since, if anything, the delocalising ability of the $\mathrm{Me_3Si}$ groups should reduce the coupling from that measured in the $\mathrm{Me(Mu)C{=}\dot{C}{-}C{\equiv}CMe}$ radical. We therefore favour the alternative view that this radical is $\mathrm{Me_3Si\dot{C}{=}C(Mu){-}C{\equiv}CSiMe_3}$ and we can compare the coupling with that measured for the structurally related $\mathrm{Me_3Si\dot{C}{=}C(Mu)Me}$ radical[2] (62.1 G). This reduction shows that there is further delocalisation occurring, and we propose that this arises *via* a 'through-space' overlap, as in the structure **1**. The only other report of a radical of this type is a tentative assignment to $\mathrm{H{-}\dot{C}{=}C(H){-}C{\equiv}CH}$, formed as a minor species in the addition of hydrogen atoms to diacetylene.[4] The couplings are given as 45 and 10 G to two inequivalent protons. However, it is difficult to make a direct comparison between these two radicals, because the radical centre must be bent (probably as in **2**) but linear in the case of **1**.

What is clear, however, is that the propensity in hydrogen (muonium or protium) addition to the diacetylene system is at the terminal positions, but the stabilisation of a radical that arises from the presence of the $\mathrm{Me_3Si}$– substituent in **1** reverses this intrinsic reactivity order and directs the addition to the adjacent position.

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