Muonium Adducts of Fulvenes

Christopher J. Rhodes,*[a] Emil Roduner,[b] Ivan Reid[b] and Toshiyuki Azuma[b]

[a] *Department of Chemistry, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, UK*

[b] *Physikalisch-Chemisches Institut der Universitat Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland*

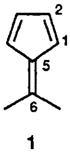
Muon avoided level crossing spectroscopy (ALC) shows that in muonium atom addition to fulvenes, radicals are formed exclusively by addition to the 1 and 2 positions.

The unique properties of fulvenes **1** have long been a source of great interest to chemists: in particular, their large dipole moments,[1] which are very sensitive to the effect of substitution at the exocyclic 6-position,[2] and may be viewed in terms of the relative importance of the dipolar structure **2**. Results from NMR spectroscopy indicate that electron-releasing substituents at position 6 increase the cyclopentadienide character of the 5-membered ring.[3] Spectroscopic measurements of radicals derived from fulvenes are sparse, and appear to be confined to the recent characterisation of fulvene radical cations, by one of us using ESR spectroscopy,[4,5] and by Abelt and Roth from a CIDNP study.[6]

Our present interest in fulvenes concerns their reactivity towards muonium atoms which were produced during the irradiation of 6,6-dimethyl- and 6,6-diphenyl-fulvene (in ether solution) with positive muons.

Fig. 1 shows the transverse field μSR spectrum[7] recorded under these conditions from 6,6-dimethylfulvene, and it is clear that two radicals are formed [A_{μ}' (1) = 11.79, A_{μ}' (2) = 22.82 G; these couplings are divided by the ratio of muon/proton magnetogyric ratios; $1\ \text{G} = 10^{-4}\ \text{T}$]. Their assignment is difficult, however, because there are four possible sites for addition to occur, leading potentially to the radicals **3**–**6**. In this case, a definitive assignment can only be made if the hyperfine couplings to the other magnetic nuclei present in the radicals are known, in addition to those for the muons. While estimates of additional nuclear hyperfine couplings may sometimes be obtained from the line-splittings observed in transverse magnetic fields that are sufficiently low that the muon transition frequencies are affected by the other nuclear hyperfine interactions,[7,8] this technique is not suitable for measuring small couplings and complex hyperfine patterns. We have therefore used the technique of muon avoided level crossing (ALC)[9,10] to monitor the muon–electron 'cross-polarisations' at values of the applied (longitudinal) magnetic field where muon and proton transition frequencies are matched. From these field values and the muon hyperfine couplings measured by transverse field μSR, both the magnitudes and the signs (relative to that of the muon) of the couplings to nuclei other than the muon may be determined. The ALC spectrum recorded from 6,6-dimethylfulvene (in ether solution) is shown in Fig. 2, along with a simulation obtained using the proton hyperfine couplings given in the Scheme 1. It is evident that the spectrum is reasonably interpreted in terms of muonium atom addition to the 1 and 2 positions of the fulvene ring, with the formation of the radicals **3** and **4** in the ratio 1.4 : 1.0.

Since fulvene is an isomer of benzene, the adducts **3** and **4** may be regarded as (substituted) isomers of the cyclohexadienyl radical. However, the large hyperfine couplings (*ca.* 48 G) measured for the 'methylene' protons in this system are not manifested in the radicals **3** and **4** because these do not contain the required structural feature of mutually reinforcing interactions with two adjacent positions of relatively large spin density (the 'Whiffen effect').[11] Radical **3** is related to the pentadienyl radical **7**[12] and the overall spin distribution is closely analogous, as shown by the similar pattern of coupling constants (Scheme 1). From the spin population at position 2 (**1**) (0.383),[13] and by assuming that the dihedral angles between the C–H/C–Mu bonds and the density axis of the atomic p-orbital contributing to the SOMO are 30°, a coupling of 15.5 G is predicted, which is substantially greater than that observed (10.3 G); however, there is also an adjacent position (5) of negative spin density, which may be estimated at −0.130, on the basis of the degree of spin correlation normally found in alternant radicals[14]. If a Q value of 29.25 G (for a freely rotating Me group, where $\langle\cos^2\theta\rangle = 0.5$) is used,[15] and the interaction with the two adjacent positions is taken as being proportional to the simple addition of their spin densities, a proton coupling of $(0.383–0.130) \times 27 \times \cos^2 30°/0.5 = +11.1$ G is predicted, in reasonable agreement with the experimental value (+10.3 G).



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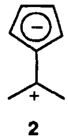

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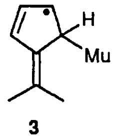

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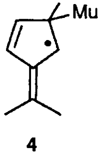

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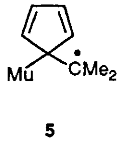

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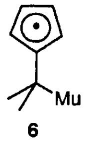

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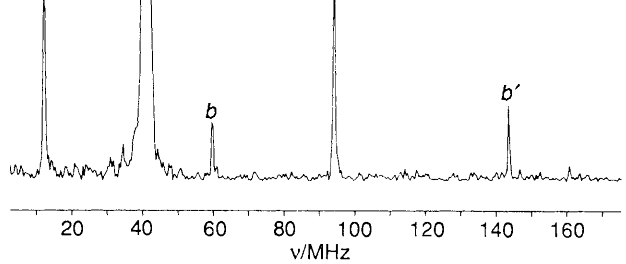


Fig. 1 Transverse field μSR spectra recorded from 6,6-dimethylfulvene. Peaks marked (*a*) are from radical **3**, (*b*) from radical **4**, (*c*) from muons in diamagnetic environments.

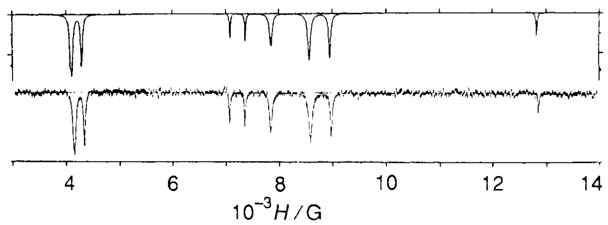
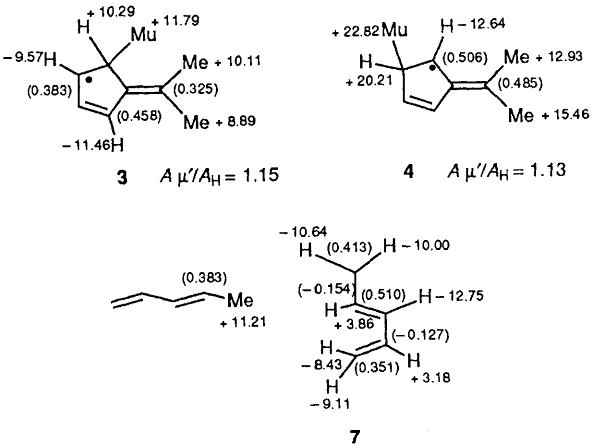


Fig. 2 Avoided level crossing (ALC) spectrum from 6,6-dimethylfulvene in diethyl ether solution (1 : 6); the upper trace is the simulation based on a mixture of **3** and **4**; the lower trace is the experimental spectrum



Scheme 1 Coupling constants and (spin-populations) for fulvene–muonium adducts and related radicals. Spin populations obtained using $Q = -25$ G for α-protons[13] and $Q = +29.25$ G for Me protons.[15]

The radical **4** is a 'cross-conjugated' allyl radical, and the couplings from protons interacting in the effectively 'localised' allylic radical system (at the 6,5,1 positions) are typical for normal open-chain allyl radicals.[16] The spin density at position 1 is 0.506 and so we anticipate a coupling to the CHMu proton of $27 \times 0.506 \times \cos^2 30°/0.5 = 20.48$ G. This is very close to that observed (20.21 G) and so the (negative) spin density at the 3-position (**1**) is negligible. The hyperfine isotope ratios ($A\mu/Ap$) for **3** and **4** (Scheme 1) are unexceptional and within the range established previously for conformationally fixed radicals.[17]

Although we have not measured an ALC spectrum of 6,6-diphenylfulvene, by analogy with the above results, it appears most likely that it is the 6,6-diphenyl versions of **3** ($A\mu' = 7.13$ G) and **4** ($A\mu' = 14.93$ G) that are formed in the transverse field experiment, but with reduced muon hyperfine couplings because of the additional spin delocalisation onto the phenyl substituents.

We note that from a mixture of kinetic results and qualitative reasoning, it was proposed that addition of thiyl radicals to fulvenes[18] takes place at the ring, rather than the exocyclic 6-position, and that addition to position 1 was most probable. The present results may be taken to support this view of radical addition but show that the position 2 is also activated.

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