The first observation of a muonium–carbonyl adduct with a negative muon coupling constant

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Muonium atom addition to cyclopent-4-ene-1,3-dione I leads to the adduct radical II; in contrast with all other muonium adducts of carbonyl (C=O) compounds so far studied, in which the isotropic muon coupling is of positive sign, the temperature dependence of the muon coupling in II reveals that its sign is negative; this may be explained as a consequence of the electronic 'push–pull' interaction within the MuO–C–C=C–C=O system, which reduces the out-of-plane vibrational amplitude of the muon by increasing the MuO–C/MuO=C partial π-bond character.

There have been a number of studies[1–12] made of free radicals formed by addition of the light hydrogen isotope, muonium (a hydrogen atom with a positive muon as its nucleus) to compounds containing a single carbonyl (C=O) group, which include aldehydes, ketones, esters and amides. All these radicals possess the common structural feature of a muonium atom which is bound close to the radical plane ($C^{\bullet}$–O–Mu), but which can make vibronic (out-of-plane) excursions from it: the observed coupling is now a compromise between two contributions; one providing negative spin density in the muonium 1s orbital, arising from spin polarisation of the O–Mu bond by spin density at the oxygen atom, and the second, which is a positive transfer of spin density to the muon, as the out-of-plane vibration permits a degree of overlap with the spin bearing formal carbon $2p_z$ orbital. This may be expressed by, $A(\mathrm{Mu}) = B_0 + B_1 \cdot f(T)$, with B_0 being of negative sign.

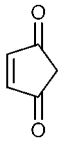
In consequence, the muon couplings measured in carbonyl adducts are all small (which contrasts the large, positive, values normally found in carbon centred radicals[13,14]), and in all examples so far investigated are of positive sign, as deduced from the fact that the couplings all increase with increasing temperature,[1,2] and so the positive term $B_1 \cdot f(T)$ is dominant.

Recently,[1] we reported a theoretical study of the muonium adduct of a 1,2-dicarbonyl compound (biacetyl, MeCOCOMe), which aimed to explain its extremely small experimental coupling of 1.9 MHz (at 294 K), but were unable to decide entirely between the possible effects (i) and (ii) mentioned below, and now appeal to experimental evidence. To this end, we have measured the temperature dependence of the isotropic muon coupling (Table 1) which is positive, and therefore shows[1,2] that the sign of the coupling is also positive; so although the two contributions are now almost equal, the transfer of positive spin density still wins, but the very low value of the coupling means that the muon is more closely confined to the radical plane than in all cases of radicals derived from a *single* carbonyl group. The presence of the second C=O group, therefore, has a profound effect on the electronic structure of the radical. There are two possible reasons for this: (i) the adduct has adopted an s-*cis* geometry, with an intramolecular hydrogen (Mu) bond between the two oxygen atoms (**III**); (ii) the s-*trans* conformation of the parent biacetyl molecule is preserved, but the electronic 'push–pull' character of the Mu–O–C–C=O system confines the muon by increasing the O–C/O=C π-bond character of the Mu–O–C unit (it is this which determines the potential barrier to the out-of-plane excursion of the bound muon[1,2]).

Table 1 Temperature dependences of the muon coupling in the adduct radicals formed from cyclopent-4-ene-1,3-dione **I**[a] and biacetyl[b]

Coupling[a]/ MHz	T/K	Coupling[b]/ MHz	T/K
5.42	242	1.64	284
4.68	255	1.90	294
4.16	265	2.06	297
3.40	275	2.29	303
2.83	285	4.45	323
2.26	299	5.65	335
1.81	303		
1.58	308		

In order to examine the influence of a potential 'through-bond', π-electronic effect, in the absence of intramolecular hydrogen bonding, we chose a dicarbonyl substrate, cyclopent-4-ene-1,3-dione **I**, in which the carbonyl groups are in communication *via* a C=C bond, but are fixed mutually *trans* by the bridging methylene group, so that intramolecular H(Mu)-bonding is impossible.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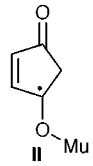
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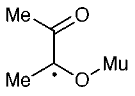
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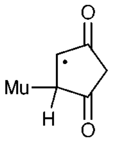
IV

Two radicals were detected using the transverse-field muon spin rotation (TF-MuSR) method[13,15] (Fig. 1): the desired carbonyl adduct **II**, for which the coupling measured as a function of temperature is shown in Table 1, and the C=C adduct **IV** with a coupling of 384 MHz measured at 299 K; the relative yields are 0.35 (C=O) and 0.65 (C=C).

It is quite clear that the coupling decreases in absolute magnitude as the temperature increases—the first example of such behaviour for a muonium/carbonyl adduct. Since the out-of-plane vibrational amplitude of the muon increases on heating, and so the interaction with positive spin density must also increase, the overall muon hyperfine coupling constant must be of *negative* sign (the term B_0 being dominant), becoming more positive at the higher temperature. This means that the O=C π-bond character of the Mu–O–C group can be significantly enhanced by the electronic effect alone, and so an intramolecular hydrogen bond is not required to explain the unexpectedly small coupling either in this or in the biacetyl/muonium adduct; indeed, the effect is greatest in the present example, probably owing to its more extensive conjugation.

This electronic system, which is unusual for a free radical, is now the subject of calculations at various levels of theory in an effort to probe their relative application in the elucidation of

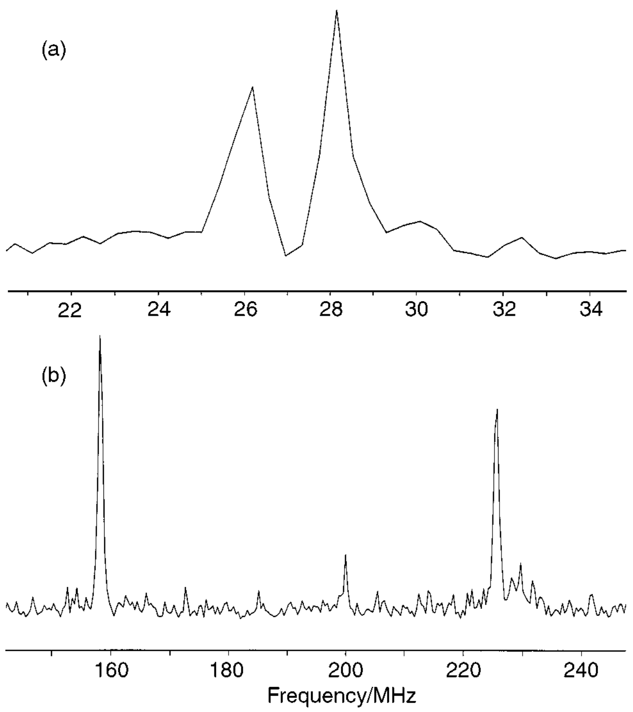

Fig. 1 Transverse-field MuSR spectrum of radicals formed by muonium atom addition to **I** at 299 K, the low-frequency region (a) corresponding to **II** while that (b) at much higher frequencies corresponds to **IV**.

detailed electronic and vibrational effects in organic free radicals.

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