

## AN INVESTIGATION OF CAPTO-DATIVE INTERACTIONS IN MUONATED CYCLOHEXADIENYL RADICALS.

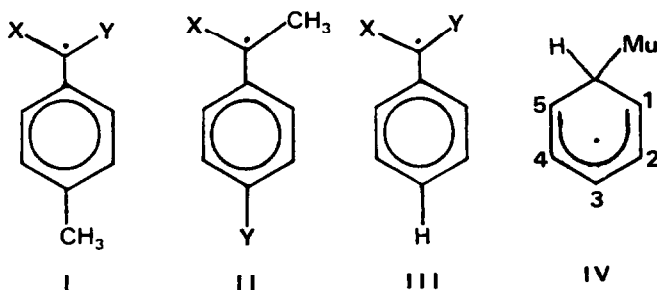
Christopher J. Rhodes,\*  
School of Chemistry, Thames Polytechnic, Wellington Street, Woolwich,  
London. SE18 6PF., U.K.

Emil Roduner,  
Physikalisch-Chemisches Institut der Universitat Zurich, CH-8057, Zurich,  
Switzerland.

**Abstract:** On the basis of the muon hyperfine coupling constants, it is concluded that the pairs of substituents in cyclohexadienyl radicals operate on the spin-density distribution in a "cpto-dative" manner, as they do in benzyl radicals, when direct conjugation with the radical centre is possible; however, for other arrangements of the substituents, opposing effects are found.

Within the important area of "radical stabilisation" a topic of current interest is that of "cpto-dative" stabilisation, in which it is proposed that the combined stabilising action of an electron releasing and an electron withdrawing substituent on a radical centre is greater than the sum of their individual effects (synergetic); and furthermore, that the combined action of two substituents of the same kind (i.e. either both electron releasing or withdrawing) is less than the sum of their individual effects (antagonistic).<sup>1,2</sup> There is evidence both for<sup>1-4</sup> and against<sup>5,6</sup> this proposal.

On the "for" side, is a recent e.s.r. study<sup>3,4</sup> of the substituted benzyl radicals (I) - (III), in which the coupling to the CH<sub>3</sub> protons in (I) and (II), and to the para-proton in (III) is taken as a spin density probe. On the basis that spin delocalisation and radical stabilisation are related<sup>7</sup>, these couplings bear out the "cpto-dative" proposal in all three series of benzyl radical.



In order to further examine the validity of such effects in the ground state of a free radical, we have observed a number of di-substituted cyclohexadienyl radicals (IV) by the  $\mu$ SR technique,<sup>8</sup> during the irradiation of the appropriately substituted benzenes with spin-polarised, positive muons. A typical spectrum is shown in Figure 1, which demonstrates the power of the  $\mu$ SR method in allowing the simultaneous observation of a number of isomeric radicals: the corresponding e.s.r. spectrum of such a mixture of radicals would be extremely complex. The linear correlation that exists between the  $A_\mu$  couplings in the cyclohexadienyl radicals and the  $a(\alpha\text{-CH}_2)$  couplings in the benzyl radicals show that cyclohexadienyl provides an equally valid model to benzyl for probing radical substituent effects.

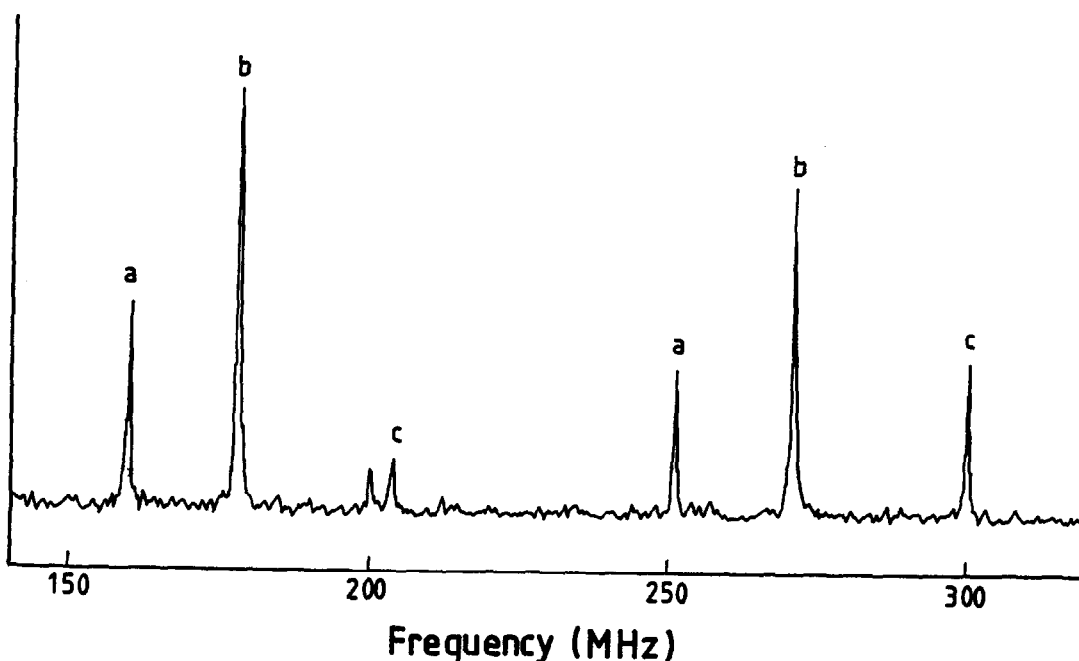


Figure 1. Transverse field uSR spectrum of isomeric radicals formed during the irradiation of 1,3-di-methoxybenzene with positive muons: (a) 1,5 isomer, (b) 1,3 isomer, (c) 2,4 isomer.

Assuming only a cumulative effect of the substituents, we would expect the relation (1) to hold:

$$A_\mu = A_\mu' \prod_x (1 - \Delta_x) \quad \dots \dots \dots (1)$$

where  $A_\mu$  is the muon coupling for the substituted radical,  $A_\mu'$  is the coupling for the unsubstituted case (derived from benzene itself), and  $\Delta_x$

is a delocalisation parameter similar to those previously derived for benzyl radicals,  $\Delta S$  and  $\sigma'$ , from references 3,4 and 6. However, we find that we can obtain better agreement with the experimental  $A_{\mu}$  values if we modify (1) by the addition of a substituent interaction parameter  $\Delta_{xy}$ , as in (2):

$$A_{\mu} = A_{\mu}' \prod_X (1 - \Delta_X) \prod_{XY} (1 - \Delta_{XY}) \dots \dots \dots (2)$$

$\Delta_{xy}$  values are collated in Table 1 for various substitutions.

Table 1. Parameters ( $\Delta_{xy}$ ) for the interaction of two substituents in the cyclohexadienyl radical in units of  $100\Delta_{xy}$ .

Position of X,Y. <sup>a</sup> (Defined in IV)	X=Me	F	Cl	OMe	OMe	CN
	Y=Me	F	Cl	OMe	CN	OMe
1,5	-0.13	-1.93		-2.62	+2.62	+2.62
1,2	-1.81	-1.62	-0.46	-7.07	+0.72	-2.60
1,4	+0.36	+1.12		+4.44	-1.20	-2.96
1,3	-0.45	-0.71	+0.04	-3.37	+5.17	+6.98
2,4	+0.01	-0.90		-1.45	-1.18	-1.18
2,3	-0.99	+1.53	+0.08	-2.53	-2.59	-1.37

a, Data for the F and Cl substituents are from reference 9, all other values are from the present work.

Clearly, if  $\Delta_{xy}$  is positive, then there is a synergetic interaction between the substituents, and if it is negative, then the interaction is antagonistic. We see that for the cases in which a direct conjugation is possible between the two substituents and the radical centre (i.e. 1,3 and 1,5 substitution) the "capto-dative" proposal is borne out. For all other arrangements of substituents, although there are appreciable substituent interactions, the signs of the  $\Delta_{xy}$  parameters scatter, and so the above antagonistic or synergetic expectations are not upheld.

Our results therefore support the captodative concept, but suggest that other, more complex, substituent effects may also operate, particularly when one or both of the substituents occupies a meta position. We note that it has previously been shown that meta substituents in benzyl radicals affect the spin density distribution via a polar rather than a spin delocalising effect.<sup>10,11</sup> The stabilisation of a radical may be complicated by polar influences of the substituents which change the overall electronic distribution, in addition to that resulting from spin delocalisation, and so the spin densities alone may not always account for the total effect of the substituents on the stability of the radical. Recent calculations have indicated that there is a significant inductive destabilising effect in methyl radicals substituted with electron withdrawing groups, but which

falls as the substituent is removed from the radical centre in a delocalised system, allowing the spin delocalisation effect to dominate.<sup>12</sup>

#### References.

- (1) H.G.Viehe, Z.Janousek, R.Merenyi and L.Stella, *Acc. Chem. Res.*, 1985, 18, 148.
- (2) H.G.Viehe, R.Merenyi, L.Stella and Z.Janousek, *Angew. Chem., Int. Ed. Engl.*, 1979, 18, 917.
- (3) L.Sylvander, L.Stella, H.-G.Korth and R.Sustmann, *Tetrahedron Lett.*, 1985, 26, 749.
- (4) H.-G.Korth, P.Lommes, R.Sustmann, L.Sylvander and L.Stella, in 'Substituent Effects in Radical Chemistry', H.G.Viehe, Z.Janousek and R.Merenyi, Eds., Reidel, Dordrecht, 1986.
- (5) M.Zamkanej, J.H.Kaiser, H.Birkhofer, H.-D.Beckhaus and C.Ruchardt, *Chem. Ber.*, 1983, 116, 3216.
- (6) H.Birkhofer, J.Hadrich, H.-D.Beckhaus and C.Ruchardt, *Angew. Chem., Int. Ed. Engl.*, 1987, 26, 573.
- (7) J.M.Dust and D.R.Arnold, *J. Am. Chem. Soc.*, 1983, 105, 1221.
- (8) E.Roduner and H.Fischer, *Chem. Phys.*, 1981, 54, 261.
- (9) E.Roduner, G.A.Brinkman and P.W.F.Louwrier, *Chem. Phys.*, 1982, 73, 117.
- (10) D.D.M.Wayner and D.R.Arnold, *Can. J. Chem.*, 1985, 63, 2378.
- (11) C.J.Rhodes, D.Phil thesis, University of Sussex, 1985.
- (12) D.J.Pasto, R.Krasnansky and C.Zercher, *J. Org. Chem.*, 1987, 52, 3062.

(Received in UK 28 January 1988)