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ENDOR INVESTIGATIONS ON THE CAPTO-DATIVE STABILISATION OF TRIPHENYLMETHYL RADICALS

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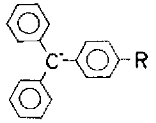
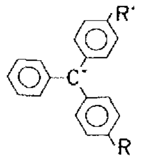
Summary. The influence of polar substituents on the spin density in monosubstituted triphenylmethyl radicals 1 is less or equal to that of the unpolar phenyl group. The influence of two equal substituents in radicals 2 is less than additive, radicals 2 with electron accepting and donating substituents show a small capto-dative effect.

The influence of polar substituents on the stability of free radicals has found growing interest during the last years.[1] Especially, a "capto-dative" stabilisation by the combination of electron accepting and donating substituents is discussed intensively and controversially.[2] The first known and thoroughly studied stable free radical is the triphenylmethyl radical.[3] It is stabilized by the introduction of one or two substituents as could be shown by investigation of the thermal equilibrium between radicals 1 and 2 with their dimers.[4] The degree of dissociation of the dimers with R/R′= tBu/CF_3, tBu/CN and OMe/CN shows a weak synergetic effect.[4] Spin density distributions in radicals 1 and 2 should sensitively depend on substituents.[5] As the complex ESR spectra could not be analyzed in detail, the ENDOR technique has been used which allows the investigation of radicals with many inequivalent nuclei,[6] and the influence of substituents on the spin density distribution in radicals 1 and 2 will be described.

1:



2:



R, R′ = tBu-, -OMe, -OPh
-CF_3, -CN, -COPh

In Table 1, the splitting parameters of radicals 1 are given. a_o, a_m and a_p are proportional to the spin density at the central carbon atom and, therefore, a direct measure of the spin drawing or releasing effect of the substituent.[7-9] As the ortho and meta splittings are not resolved in any case, only the para proton splittings will be discussed in the following. The influence of the donor substituents on the spin density distribution is small, that of the accep-

Table 1. ENDOR data of radicals 1 at 200 K in toluene (a)

R	a_p (b)	a_o	a_m	a_R	ΔH (c)	ΔS (d)
OMe	2.93 (1)	2.58 (e)	1.02/1.16	H: 0.31		
H (f)	2.86	2.61	1.14		10.7	20
tBu	2.85 (1)	2.60	1.14	H: 0.11	10.2	20
OPh	2.84 (2)	2.60 (e)	1.12 (e)	H: 0.05		
CF_3	2.76 (3)	2.54 (e)	1.13 (e)	F: 4.68	10.5	21
Ph (f)	2.72	2.48/2.72	1.10/1.21	H: 0.19/0.49		
CN	2.62 (2)	2.38/2.86	1.06/1.16	N: 0.47 (g)	10.0	21
COPh	2.60 (1)	2.41/2.60	1.08/1.23	H: < 0.02	10.2	23

Table 2. ENDOR data of radicals 2 at 200 K in toluene (a)

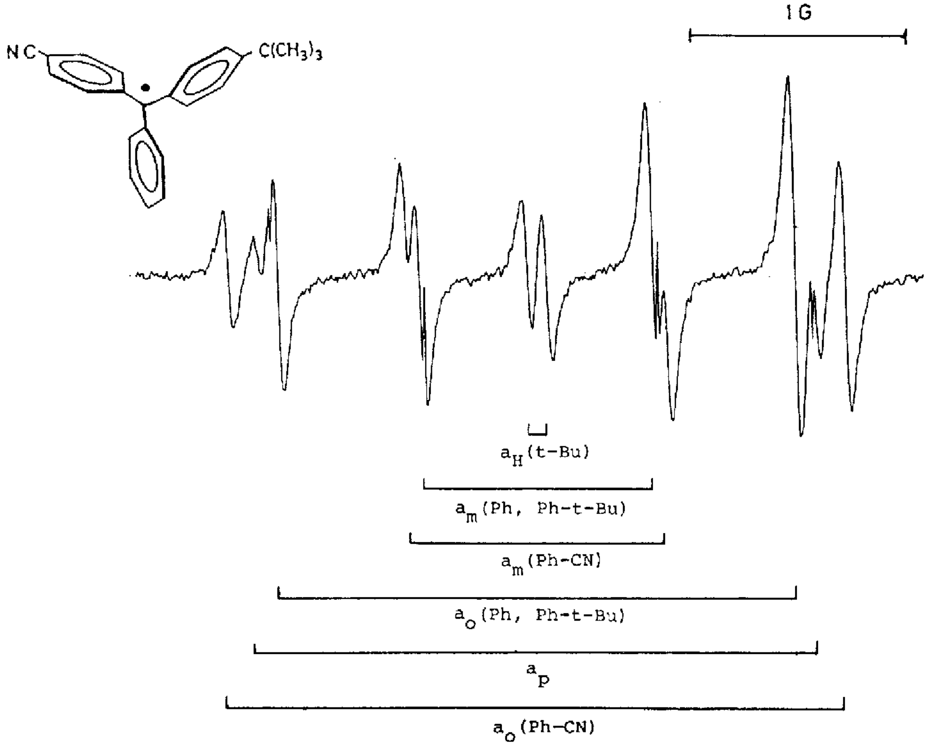
R/R′	a_p (b)	a_o	a_m	a_R	$a_{p,calc}-a_p$	ΔH(c)	ΔS(d)
OMe/OMe	2.92(1)	2.57 (e)	1.04 (e)	H: 0.32	0.08	7.1	12
tBu/tBu	2.88(2)	2.59	1.13	H: 0.10	-0.04	8.2	17
OPh/OPh	2.83(2)	2.62 (e)	1.10	H: 0.05	-0.01	9.4	18
CF_3/CF_3	2.70(3)	2.53 (e)	1.13	F: 4.36	-0.04		
Ph/Ph (f)	2.60	2.38/2.60	1.07/1.17	H:0.19/0.46	-0.01	6.8	16
CN/CN	2.64(3)	2.30/2.64	1.12 (e)	N: 0.42(g)	-0.26		
COPh/COPh	2.46(1)	2.28/2.64	1.04/1.16	H: < 0.02	-0.10	7.6	16
tBu/CF_3	2.73(1)	2.52 (e)	1.13 (e)	F: 4.73 H: 0.09	0.02(0.06)		
tBu/CN	2.60(1)	2.41/2.88	1.07/1.21	H: 0.09	0.00(0.16)	7.9	17
OMe/CN	2.53(1)	2.35/2.85	0.96/1.20	H: 0.32	0.15(0.25)		

(a) Splitting parameters in G, 1G = 2.8025 MHz. (b) Errors in parentheses. (c) Dissociation enthalpy of the dimer in kcal/mol.[4] (d) Dissociation entropy of the dimer in cal/mol·K.[4] (e) Further splittings not resolved. (f) Taken from 10. (g) ESR data.

tor substituents larger and in the order of the unpolar phenyl group. Dissociation enthalpies and entropies of the dimers are added.[4] They do not show any significant dependence on the substituents.

In Table 2, ENDOR data of radicals 2 and dissociation enthalpies and entropies of the corresponding dimers are listed. Additionally, differences between expected and observed a_p values are given calculated with Fischer′s formula [7] and the a_p values from Table 1. An ENDOR spectrum of 2 (R/R′ = tBu/CN) is shown in Figure 1. With R = R′, the second substituent has a smaller influence than the first one. In the case of OMe and CN substituents, the effect is even

Figure 1. ENDOR spectrum of **2** (R/R′ = tBu/CN) at 200 K in toluene



smaller than that of a single substituent. Radicals **2** with R/R′ = tBu/CF_3 and tBu/CN show additivity of the substituent effects. The capto-dative combination R/R′ = OMe/CN leads to a greater than additive reduction of the spin density of the unsubstituted ring. For calculating the numbers in parentheses, half the differences between the a_p values of the symmetrically disubstituted radicals **2** and 2.86 G have been used. The weakening effect of two substituents is eliminated by this procedure.[4] By doing this, the two radicals with R/R′ = tBu/CF_3 and tBu/CN show a capto-dative effect, too. The dissociation enthalpies and entropies are not correlated with the a_p data.

The stabilisation δ(SE) caused by the substituents might be estimated from the splitting parameters in the following way

$$\delta(\mathrm{SE}) = 25 \quad [1 - a_p(R,R')/a_p(R,R'=H)] \quad \mathrm{kcal/mol} \qquad (I)$$

An analogous relation has been given for the benzyl radical .[11] It will be extended here for radicals **1** and **2** by taking into account the slightly higher spin density ρ at the central carbon atom of the triphenylmethyl radical (ρ = 0.68[12]) compared with that of the benzyl radical (ρ = 0.58[13]).[14] From (I), δ(SE) values up to 3.6 kcal/mol are calculated which are in the same order of magnitude as the deviations within the ΔH values (<4 kcal/mol). The capto-dative stabilisation energy of radicals 2 is 0.5 - 2 kcal/mol. This is comparable with the variations of ΔH in Table 2. Besides the capto-dative stabilisation of radicals 2, there obviously are other factors determining the magnitude of ΔH.[15]

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