

THE CAPTO-DATIVE SUBSTITUENT EFFECT ON BENZYLIC RADICALS ESR HYPERFINE SPLITTINGS.  
AN EVALUATION OF THE EXTRA STABILIZATION BASED UPON SPIN DELOCALIZATION<sup>1,2</sup>

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Abstract: Appropriate hyperfine splittings in ESR spectra of disubstituted (cyano/methoxy) benzylic radicals were compared with the corresponding values of monosubstituted ones. On the basis of the dependence of radical stabilization on spin delocalization, it is concluded that captodative substitution implies a synergetic substituent effect on radical stabilization. On the contrary, an antagonistic effect is observed in the case of two identical substituents.

A few years ago, Viehe and coworkers<sup>3</sup> have postulated that the combined action of acceptor and donor substituents on a radical center should lead to an enhanced stabilization compared to acceptor/acceptor or donor/donor substitution. From that time, the captodative substituent effect has convincingly emerged as a useful concept in organic synthesis via radicals by virtue of its selective applications<sup>4</sup>. Furthermore, the concept has stimulated theoretical<sup>5</sup> and experimental<sup>6</sup> investigations to analyse the term "stabilization" more thoroughly. An ESR-spectroscopic kinetic study<sup>7</sup> showed, that captodative substituted methyl radicals do not possess kinetic stabilization, i.e. longer life times than other transient radicals. If the special features of captodative substituted radicals do not derive from kinetic effects then the question about their thermodynamic stabilization remains to be answered. Rotational barriers in substituted allylic radicals<sup>6i</sup> and bond dissociation energies in 1,2-diphenyl ethanes<sup>6h</sup> provided some quantitative data on the combined effect of a donor and an acceptor substituent and showed that the effects were at least additive.

Desirable would be the evaluation of substituent effects in the ground state of radicals. As the measurement of spin density distribution by ESR spectroscopy constitutes a very small perturbation of the ground state it should be a good measure for this purpose, and on the basis that spin delocalization and stabilization are interrelated<sup>8</sup>, it should provide a relative substituent scale. We report here some preliminary results concerning hyperfine splittings (hfs) in the ESR-spectra of a homogeneous series of mono- and disubstituted benzylic radicals.

To reflect accurately relative spin delocalization with minimal changes in hybridization at the radical center, it seemed that the phenylogous series 1 of the well-known Fischer model<sup>9</sup> includes the most suitable radicals to be compared. The benzylic nature of these radicals avoids deviation from planarity even when the  $\alpha$ -substituent X is a good electron donor group<sup>10</sup>. It fol-

flows from the mechanism of hyperconjugation that the  $\beta$ -H hfs are proportional to the spin population of the  $\alpha$ -carbon  $2p_z$  orbital<sup>11</sup>. Therefore, it has been suggested to use the  $\beta$ -coupling constants of methyl group protons as  $\alpha$ -carbon spin density probe<sup>9,12</sup>. In general, the  $\beta$ -H hfs of a freely rotating methyl group provide a better probe for the  $\alpha$ -carbon spin density than the  $\alpha$ -H hfs because they are less sensitive to configurational or through-bond spin polarization effects<sup>13</sup>.

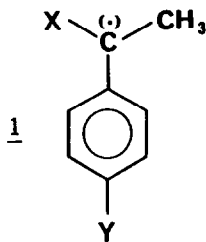
The para-substituent Y interacts significantly with the radical center and is away far enough to influence only the spin delocalization<sup>8</sup>. Therefore, variations in the  $\beta$ -H hfs should reflect changes in spin delocalization, and an increased spin delocalization should indicate an increased radical stabilization.

Assuming the relatively small values of the stabilization energies of an  $\alpha$ -methoxy ( $\sim 1.5$  kcal/mol)<sup>14</sup> and of an  $\alpha$ -cyano substituent ( $\sim 5.5$  kcal/mol)<sup>6h</sup> on benzyl radical, the determination of their synergetic or antagonistic action through phenyl group requires a very accurate and precise method. The data presented here show that this prerequisite has been fulfilled.

The benzylic radicals were generated at low temperature by ultraviolet-irradiation in the ESR-cavity of a flowing solution containing the parent molecule, di-tert-butylperoxyde and chlorobenzene (1:1:1)<sup>15</sup>. The ESR-spectra were analyzed manually and the hfs were then refined by computer simulation. From the  $\beta$ -H hfs, listed in table 1, we can define (eq. 1), in analogy to Fischer's increments<sup>9</sup>  $\Delta$  and Arnold's substituent constants<sup>8</sup>  $\sigma_\alpha^\bullet$ , experimental delocalization parameters  $S^{\text{exp}}$  for the homogeneous series of mono and disubstituted radicals 1. For the unsubstituted benzylic radical 1a,  $S^{\text{exp}}$  is zero and the value increases with the stabilizing power

Table 1 -  $\beta$ -H hfs and delocalization parameters in benzylic radicals 1.

Radical	X	Y	$a_{\text{H}}^{\text{CH}_3}$ <sup>a</sup> (G)	$S^{\text{exp}}$ <sup>b</sup>	$S^{\text{calc}}$ <sup>c</sup>	$\Delta S$ (%) <sup>d</sup>
<u>1a</u>	H	H	17.70	0		
<u>1b</u>	H	OMe	17.25	0.025		
<u>1c</u>	H	CN	16.90	0.045		
<u>1d</u>	CN	H	16.10	0.090		
<u>1e</u>	CN	CN	15.90	0.102	0.131	-22
<u>1f</u>	OMe	OMe	15.75	0.110	0.146	-25
<u>1g</u>	OMe	H	15.50	0.124		
<u>1h</u>	CN	OMe	14.85	0.161	0.113	+42
<u>1i</u>	OMe	CN	13.95	0.212	0.163	+30



<sup>a</sup> Values are believed to be accurated  $\pm 0.02$  G.

$$^b S_{XY}^{\text{exp}} = 1 - \frac{a_{XY}}{a_{\text{HH}}} \quad (\text{eq. 1})$$

$$^c S_{XY}^{\text{calc}} = 1 - (1 - S_{\text{XH}}^{\text{exp}})(1 - S_{\text{HY}}^{\text{exp}}) \quad (\text{eq. 2})$$

$$^d \Delta S = \frac{S_{XY}^{\text{exp}} - S_{XY}^{\text{calc}}}{S_{XY}^{\text{calc}}} \quad (\text{eq. 3})$$

of the substituent or of the couple of substituents. It is evident from these data, that captodative substitution has more stabilizing power than acceptor/acceptor or donor/donor substitution.

Furthermore, for the disubstituted radicals we can then calculate  $S^{\text{calc}}$  (eq. 2) which represents the superimposed effects of two independent substituents. These values are significantly higher than the corresponding  $S^{\text{exp}}$  values in the cases of radicals with two identical substituents but are lower in the cases of captodative radicals. Thus,  $\Delta S$  (eq. 3) reveals a synergetic effect of substituents if positive and an antagonistic one if negative.

Although phenology attenuates the substituent effect of Y, the variations observed in  $\Delta S$  (-25 to +42%) certainly are significant<sup>16</sup>. More important should be the synergetic or antagonistic effect of two substituents directly bonded to the same atom. This prediction is obviously verified by the study of another phenologous series 2 of the Fischer model<sup>9</sup>. In radicals 2, X and Y substituents are in  $\alpha$ -position to the benzylic radical center and the H hfs of the freely rotating para-methyl group is used as  $\alpha$ -carbon spin density probe. This model was not considered a priori as the most suitable owing to a possible steric interaction between X and Y which can cause ring-twisting and can therefore influence the hfs. Considering the results listed in table 2 it appears that this prejudice does not hold.

Table 2 - H hfs of *para*-methyl group and delocalization parameters in benzylic radicals 2.

Radical	X	Y	$a_{\text{H}}^{\text{CH}_3(\text{G})}$	$S^{\text{exp}}$	$S^{\text{calc}}$	$\Delta S(\%)$
<u>2a</u>	H	H	6.53	0		
<u>2b</u>	OMe	OMe	6.40	0.020	0.183	-89
<u>2c</u>	H	CN	5.92	0.093		
<u>2d</u>	H	OMe	5.90	0.096		
<u>2e</u>	CN	CN	5.90	0.096	0.177	-46
<u>2f</u>	CN	OMe	4.44	0.320	0.180	+78

In conclusion, the spin delocalization in captodative radicals is markedly increased - in comparison with a pure additional superposition of "capto" and "dative" effects. This synergetic effect is even more significant as two identical substituents do not lead to an additive influence of the substituents but reveal an antagonistic effect. This characteristic of the captodative substitution can be rationalized using a stepwise perturbational (PMO) approach<sup>3b,5a</sup> or simply visualised by additional zwitterionic valence-bond resonance structures<sup>3b,4</sup>.

Synergetic stabilisation by captodative substitution is not revealed just in benzylic radicals but also in allylic ones<sup>61</sup>, in triplet state diphenyl carbenes<sup>6b</sup> and in many other contexts<sup>4</sup>.

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## References and notes

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- 15 - The majority of spectra were recorded at  $-40^{\circ}\text{C}$  with a Bruker ER-420 X-band spectrometer equipped with a variable temperature unit. A 1-kW Hg/Xe high-pressure lamp (Hanovia 977 B-1) was used for irradiation. The synthesis and characterisation of the parent molecules will be described in a forthcoming full paper.
- 16 - Considering the  $\beta\text{-H}$  hfs values to be accurate to  $\pm 0.02$  G, the precision in  $\Delta S$  is about 4%.

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