

## Localized triplet diradicals as a probe for electronic substituent effects in benzyl-type radicals: The $\Delta D$ scale

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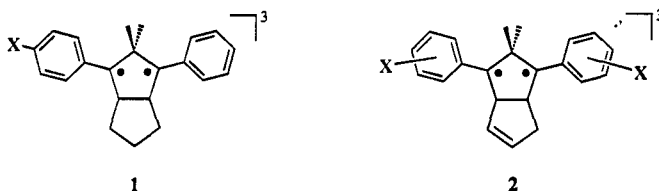
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### Abstract

The  $D$  parameter, readily determined by EPR spectroscopy, is a sensitive function of the average distance  $r$  of separation between the unpaired electrons in the localized triplet 1,3-diradicals **2** ( $D \propto 1/r^3$ ). For convenience, we have defined the difference between the  $D$  values of the benzylic substituent  $X$  and the parent system ( $X = H$ ), i.e.  $\Delta D = D_H - D_X$ , as a measure of spin delocalization by the aryl group at the radical site. The additivity of the  $\Delta D$  values of the monosubstituted diradicals **1** versus the symmetrically disubstituted diradicals **2** demonstrates that such triplet diradicals can be described as a composite of two geometrically fixed cumyl radical fragments. The  $D$  parameter correlates well with the experimental hyperfine coupling constants ( $a_\beta$ ), with the calculated  $\alpha$  spin densities ( $\rho_\alpha$ ), and the calculated resonance stabilization energies (RSE) for substituted cumyl radicals. These results manifest that the novel  $\Delta D$  scale constitutes a reliable spectral tool to determine electronic substituent effects in benzyl-type radicals and may serve as a probe to assess the importance of polar substituent effects in chemical  $\sigma_{\text{rad}}$  scales.

Triplet 1,3-diradicals can be easily generated photolytically at low temperatures in rigid glass matrices from the corresponding azoalkane precursors [1]. The EPR spectroscopy of such diradicals affords the zero-field splitting (ZFS) parameters  $D$  and  $E$  [2]. The former is a measure for the electronic spin-spin separation ( $D \propto 1/r^3$ ), the latter describes the symmetry and, thus, the conformation of the paramagnetic species and equals nearly zero for planar triplet diradicals [2].

We have investigated the electronic substituent effects on the  $D$  parameter in the localized triplet 1,3-diradicals **1** (monosubstituted) and **2** (symmetrically disubstituted), for which  $X$  represents a large variety of *para* and *meta* substituents of such previously difficult to handle groups as  $\text{NO}_2$ ,  $\text{NH}_2$ ,



OH, I and even  $\text{NH}_3^+$  or  $\text{O}^\cdot$ . A dependence was recognized between the  $D$  parameter and the propensity of the substituent to delocalize spin into the benzyl moiety. Therefore, we defined the  $\Delta D = D_H - D_X$  quantity, for which positive values ( $\Delta D > 0$ ) are found for spin-accepting substituents, e.g. *p*- $\text{CF}_3$ , *p*- $\text{CN}$ , *p*- $\text{NO}_2$ , but also *p*- $\text{NH}_2$ , while negative values ( $\Delta D < 0$ ) are observed for spin-donating substituents, e.g. *p*-F, *p*-OCOME or *p*-OH (Table 1) [3]. Interestingly, all *meta* substituents show negative  $\Delta D$  values, which implies localization of spin at the benzylic positions in the triplet diradicals [3b].

TABLE 1: *D* Parameters and  $\Delta D$  Values of the Triplet Diradicals 2<sup>a)</sup>

<i>para</i> -X	$ D/hc $ <sup>b)</sup>	$\Delta D$ <sup>c)</sup>	<i>meta</i> -X	$ D/hc $ <sup>b)</sup>	$\Delta D$ <sup>c)</sup>
<i>p</i> -NO <sub>2</sub>	0.0414	+ 0.90	H	0.0504	0.00
<i>p</i> -CN	0.0450	+ 0.54	<i>m</i> -CF <sub>3</sub>	0.0508	- 0.04
<i>p</i> -CO <sub>2</sub> Me	0.0451	+ 0.53	<i>m</i> -NO <sub>2</sub>	0.0510	- 0.06
<i>p</i> -NH <sub>2</sub>	0.0476	+ 0.30	<i>m</i> -CH <sub>2</sub> CH <sub>2</sub> Ph	0.0511	- 0.07
<i>p</i> -CF <sub>3</sub>	0.0493	+ 0.11	<i>m</i> -Cl	0.0512	- 0.08
<i>p</i> -Cl	0.0495	+ 0.09	<i>m</i> -I	0.0513	- 0.09
<i>p</i> -NH <sub>3</sub> <sup>+</sup>	0.0496	+ 0.08	<i>m</i> -Me	0.0513	- 0.09
<i>p</i> -Br	0.0499	+ 0.05	<i>m</i> -OCOMe	0.0514	- 0.10
<i>p</i> -I	0.0500	+ 0.04	<i>m</i> -NH <sub>3</sub> <sup>+</sup>	0.0517	- 0.11
<i>p</i> -O <sup>·</sup>	0.0502	+ 0.02	<i>m</i> -CN	0.0518	- 0.14
<i>p</i> -Me	0.0502	+ 0.02	<i>m</i> -OMe	0.0519	- 0.15
H	0.0504	0.00	<i>m</i> -O <sup>·</sup>	0.0522	- 0.18
<i>p</i> -OMe	0.0509	- 0.05	<i>m</i> -NH <sub>2</sub>	0.0523	- 0.19
<i>p</i> -OH	0.0509	- 0.05	<i>m</i> -OH	0.0526	- 0.22
<i>p</i> -OCOMe	0.0515	- 0.11	<i>m</i> -C≡CPh	0.0529	- 0.25
<i>p</i> -F	0.0521	- 0.17			

a) Measured in a MTHF glass matrix at 77 K; b) values given in cm<sup>-1</sup>, accuracy > 0.0001 cm<sup>-1</sup>; c) values given in 10<sup>2</sup> cm<sup>-1</sup>,  $\Delta D = D_H - D_X$ .

Dougherty's anticipation [4] that no special electronic effects (captodative stabilization, spin polarization, etc.) should play a significant role in triplet 1,3-diradicals, is now confirmed experimentally for the first time by correlating the  $\Delta D$  values of the monosubstituted 1 with the symmetrically disubstituted triplet diradicals 2. The excellent linear correspondence (Fig. 1) with a slope of 0.55

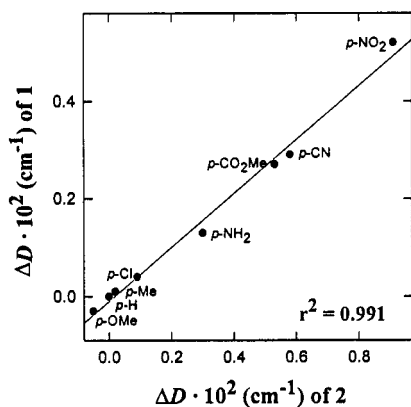


Fig. 1:  $\Delta D$  values of the monosubstituted 1 versus symmetrically disubstituted triplet diradicals 2

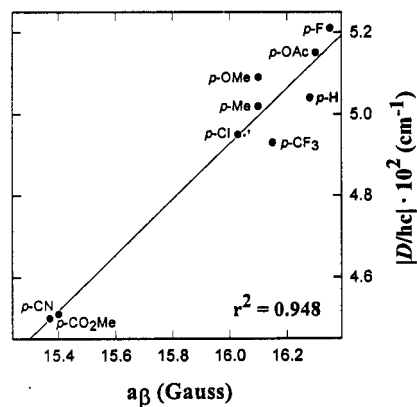


Fig. 2: *D* values of symmetrically disubstituted triplet diradicals 2 versus  $a_\beta$  hyperfine coupling constants of substituted cumyl monoradicals<sup>[5]</sup>

( $r^2 = 0.991$ ) demonstrates convincingly the additivity of the  $\Delta D$  values in such localized triplet 1,3-diradicals. As a consequence, the triplet diradicals **1** and **2** may be described as a composite of two geometrically fixed cumyl radical fragments [3c]; for the latter substituent effects have been documented [5]. As depicted in Fig. 2, in which the  $D$  parameters of the triplet diradicals **2** are plotted against the  $a_\beta$  hyperfine coupling constants of the corresponding cumyl radicals [5], the excellent linear correlation ( $r^2 = 0.948$ ) between these two EPR-spectral parameters ( $D$  and  $a_\beta$ ) demonstrates conclusively that the localized triplet 1,3-diradicals **2** are an excellent model system to assess electronic substituent effects in cumyl-type monoradicals. Our present treatment entails the first extensive experimental correlation of this kind [3a, 4b].

Since the  $a_\beta$  hyperfine coupling constant is a direct measure of the  $\alpha$  spin density ( $\rho_\alpha$ ) in cumyl radicals [5] (eq 1), the  $D$  parameter and, hence, the  $\Delta D$  values should also reflect changes in  $\alpha$  spin

$$a_\beta = A + C \cdot \rho_\alpha \cdot \cos^2 \theta \quad (1)$$

density in the cumyl radical fragment. This expectation was confirmed by a detailed quantum-chemical treatment of the magnetic spin-spin dipolar interaction for the EPR transitions in triplet diradicals. This analysis revealed, indeed, a direct dependence of the  $D$  parameter of triplet diradicals and the local spin densities  $\rho_A$  and  $\rho_B$  at the radical termini A and B (eq 2), with  $d$  as the distance between the A and B

$$D = (3\mu_o g^2 \beta^2 / 16\pi) \rho_A \rho_B / d^3 \quad (2)$$

spin sites [3c]. This relation opens up the opportunity to evaluate the electronic substituent effects in the triplet diradicals **2**. For this reason, the  $\alpha$  spin densities ( $\rho_\alpha$ ) were calculated semiempirically (PM3-AUHF/CI) for a large set of *para*- and *meta*-substituted cumyl radicals. As displayed in Fig. 3, the

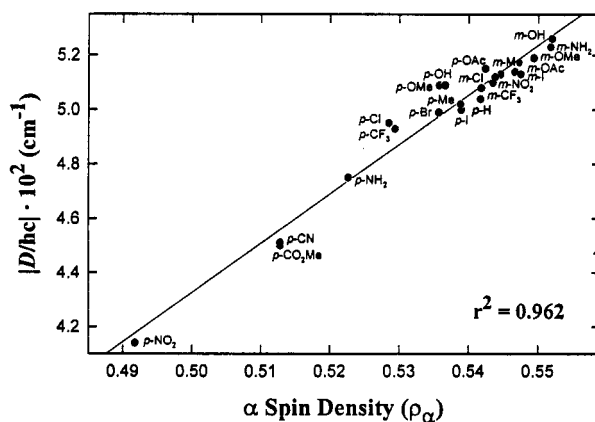


Fig. 3: Experimental  $D$  parameters of the triplet diradicals **2** versus the theoretical  $\alpha$  spin density ( $\rho_\alpha$ ) of the cumyl monoradical fragments

$D$  parameters of the triplet diradicals **2** correlate nearly perfectly ( $r^2 = 0.962$ ) with the calculated  $\alpha$  spin densities of the cumyl monoradical model systems. This good correspondence between the experimental

results ( $D$  parameter) and theoretical calculations (PM3) provides strong evidence that the *para*- and *meta*-substituted localized triplet 1,3-diradicals **2** are an excellent model system for the evaluation of electronic substituent effects in cumyl monoradicals.

To link our  $\Delta D$ -based electronic substituent effects to linear free-energy relationships (Hammett equation), an energy measure of radical stabilization is required [6]. For benzyl and cumyl radicals, Arnold [5] has reported a direct dependence between the variation in  $\alpha$  spin density ( $\rho_\alpha$ ) and the radical stabilization energy (RSE). In view of the latter correlation and since we have shown that the  $D$  parameter of the triplet diradicals **2** correlate with the  $\alpha$  spin densities in cumyl radicals, a correspondence between the substituent promoted variations of the  $D$  parameter in the localized triplet diradicals **2** and the radical stabilization energy (RSE) in the corresponding cumyl radicals was expected. Such RSE values may be conveniently assessed by computing the rotational barrier [7] as the difference (eq 3) between the energy of the  $90^\circ$  conformation (no delocalization between the radical site and the

$$RSE = \Delta H_f(90^\circ) - \Delta H_f(0^\circ) \quad (\text{eq 3})$$

aryl moiety) and the  $0^\circ$  conformation (maximal delocalization) [5,7]. These computations were performed in the same way as for the  $\alpha$  spin density (*vide supra*) by consideration only of the most interactive substituents, e.g. *p*-NO<sub>2</sub>, *p*-NH<sub>2</sub> or *m*-NH<sub>2</sub>, for which the angle dependence is exhibited in Fig. 4.

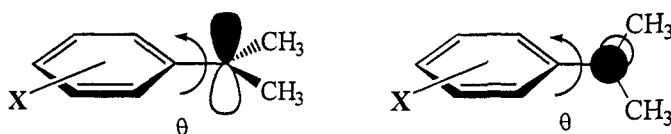


Fig. 4: Theoretical model for the computation of the resonance stabilization energy (RSE) in cumyl radicals in which  $\theta = 0^\circ$  represents full and  $\theta = 90^\circ$  no spin delocalization

In Fig. 5 are displayed the correlations of the calculated RSE values with the experimental  $D$

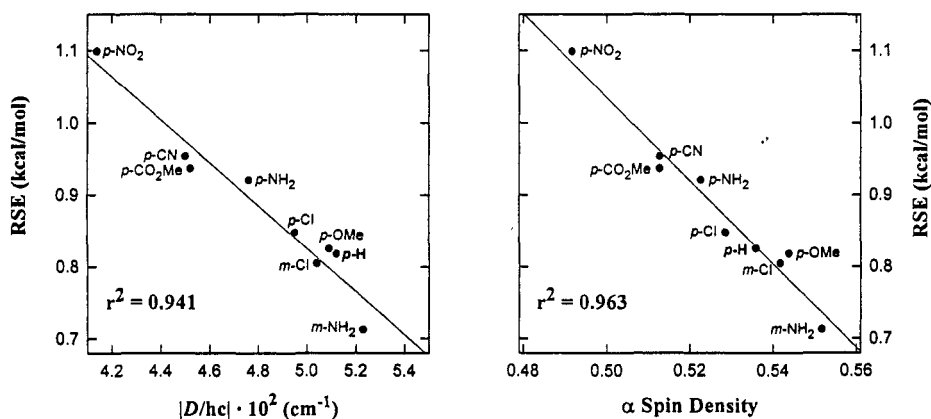


Fig. 5: Plots of the calculated RSE of cumyl monoradicals versus the  $D$  values of the triplet diradicals **2** and versus the calculated spin densities ( $\rho_\alpha$ )

parameter as well as with the calculated  $\alpha$  spin density. Both linear plots demonstrate impressively that the variations in  $\alpha$  spin density ( $\rho_\alpha$ ) of substituted cumyl radicals are related to the corresponding radical stabilization energies (RSE). Therefore, electronic substituent effects are accounted for nicely by the  $D$  parameters of the triplet diradicals **2** and, hence, by the  $\Delta D$  scale.

How does our spectroscopic  $\Delta D$  scale fare with the reported chemical  $\sigma_{\text{rad}}$  scales for electronic substituent effects in radical reactions? To date, four chemical  $\sigma_{\text{rad}}$  scales are available, based on appropriate radical reactions, which deal with electronic substituent effects on benzyl radicals [8-11]. For example, the Fisher scale [8] is based on the N-bromosuccinimide-initiated hydrogen abstraction from aryl-substituted *m*-cyanotoluenes. The most comprehensive scale is Creary's [9], which considers the relative rearrangement rates of 2-aryl-3,3-dimethylmethylenecyclopropanes. The Jackson scale [10] employs the thermolysis of dibenzylmercury compounds and the most recent one from Jiang [11] applies the dimerization rates of substituted trifluorostyrenes for this purpose. Unfortunately, the correspondence between our spectral  $\Delta D$  and the reported chemical  $\sigma_{\text{rad}}$  values is mostly poor (Fig. 6); however, in the

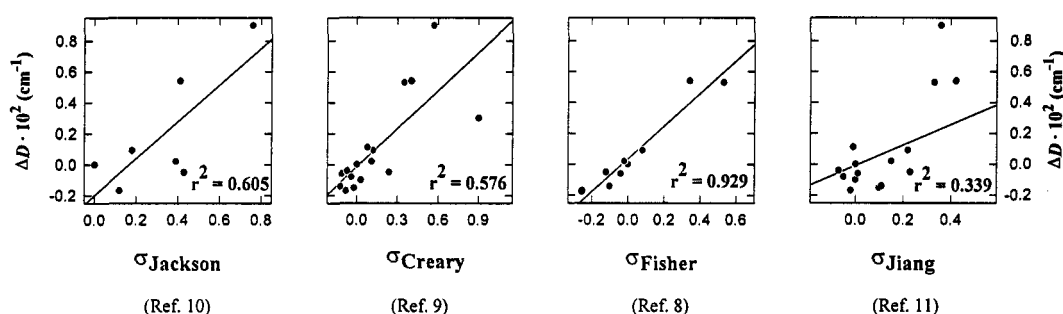


Fig. 6:  $\Delta D$  versus reported chemical  $\sigma_{\text{rad}}$  values

chemical  $\sigma_{\text{rad}}$  scales, polar contributions in the transition state (probably also in the ground state [12]) may operate, which would encumber a reliable assessment of the electronic substituent effects in radicals. To determine whether polar effects may play a role in the  $\sigma_{\text{rad}}$  scales, a two-parameter Hammett analysis (eq 4) was performed for the Creary scale ( $\sigma_{\text{Creary}}$ ), since this scale encompasses the largest set

$$\Delta D = \rho_{\text{rad}} \cdot \sigma_{\text{rad}} + \rho_{\text{pol}} \cdot \sigma_{\text{pol}} \quad (4)$$

of available substituents for comparison. Indeed, a substantial improvement in the linear correlation ( $r^2 = 0.576$  to  $0.903$ ) was obtained, when corrections for polar effects were made in terms of Hammett polar substituent constants (Fig. 7). This two-parameter analysis reveals that polar substituent effects are important in chemical radical scales, but the electronic substituent effects are predominantly radical-type in nature, as expressed by the Hammett reaction constants ( $\rho_{\text{rad}} = 1.00$  versus  $\rho_{\text{pol}} = 0.41$ ).

In conclusion, we have shown that the  $D$  parameter of localized triplet diradicals, experimentally measured by EPR spectroscopy, provides the novel spectral  $\Delta D$  scale to assess electronic substituent effects in benzyl-type monoradicals. The  $\Delta D$  values correlate well with experimental hyperfine coupling constants ( $a_\beta$ ), with the calculated  $\alpha$  spin densities ( $\rho_\alpha$ ), and the resonance stabilization energies (RSE) for cumyl radicals. A good linear correspondence is achieved between  $\Delta D$  and the chemical  $\sigma_{\text{rad}}$  values,

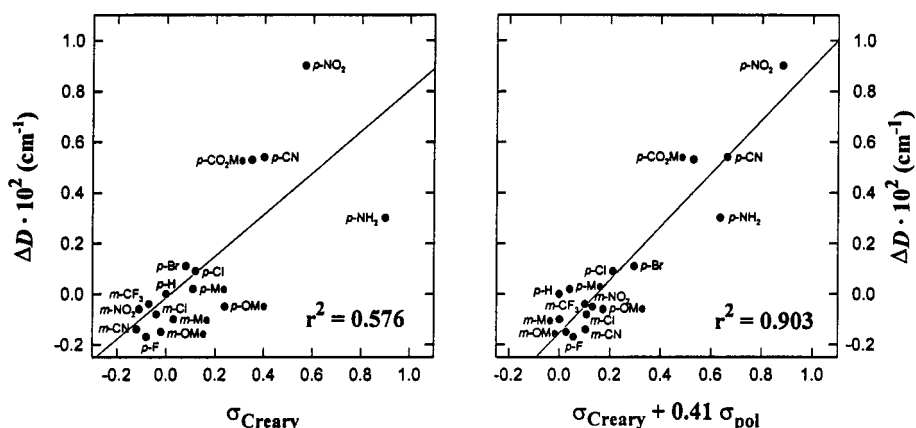


Fig. 7: Plots of  $\Delta D$  against the Creary  $\sigma_{\text{rad}}$  values ( $\sigma_{\text{Creary}}$ ) without (left) and with (right) correction for polar effects by means of a two-parameter Hammett analysis

e.g. the Creary scale, provided the polar substituent effects are corrected for by means of a two-parameter Hammett treatment. In view of the inherent difficulties to establish a generalized chemical  $\sigma_{\text{rad}}$  scale, we contend that our spectral  $\Delta D$  scale constitutes a reliable measure of electronic substituent effects in benzyl-type radicals.

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