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

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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 aryli 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 $\sigma$ 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 NO$_2$, NH$_2$, OH, I and even NH$_3^+$ or O$^-$. 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. $p$-CF$_3$, $p$-CN, $p$-NO$_2$, but also $p$-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 I: $D$ Parameters and $\Delta D$ Values of the Triplet Diradicals $2$ a)

| $\text{para-X}$ | $|D|/\text{hc}$ b) | $\Delta D$ c) | $\text{meta-X}$ | $|D|/\text{hc}$ b) | $\Delta D$ c) |
|-----------------|--------------------|--------------|-----------------|--------------------|--------------|
| $p$-NO$_2$      | 0.0414             | + 0.90       | H               | 0.0504             | 0.00         |
| $p$-CN          | 0.0450             | + 0.54       | $m$-CF$_3$      | 0.0508             | - 0.04       |
| $p$-CO$_2$Me    | 0.0451             | + 0.53       | $m$-NO$_2$      | 0.0510             | - 0.06       |
| $p$-NH$_2$      | 0.0476             | + 0.30       | $m$-CH$_2$CH$_2$Ph | 0.0511         | - 0.07       |
| $p$-CF$_3$      | 0.0493             | + 0.11       | $m$-Cl          | 0.0512             | - 0.08       |
| $p$-Cl          | 0.0495             | + 0.09       | $m$-I           | 0.0513             | - 0.09       |
| $p$-NH$_3^+$    | 0.0496             | + 0.08       | $m$-Me          | 0.0513             | - 0.09       |
| $p$-Br          | 0.0499             | + 0.05       | $m$-OCOMe       | 0.0514             | - 0.10       |
| $p$-I           | 0.0500             | + 0.04       | $m$-NH$_3^+$    | 0.0517             | - 0.11       |
| $p$-O$^-$       | 0.0502             | + 0.02       | $m$-CN          | 0.0518             | - 0.14       |
| $p$-Me          | 0.0502             | + 0.02       | $m$-OMe         | 0.0519             | - 0.15       |
| $p$-OMe         | 0.0509             | - 0.05       | $m$-O$^-$       | 0.0522             | - 0.18       |
| $p$-OH          | 0.0509             | - 0.05       | $m$-NH$_2$      | 0.0523             | - 0.19       |
| $p$-OCOMe       | 0.0515             | - 0.11       | $m$-OH          | 0.0526             | - 0.22       |
| $p$-F           | 0.0521             | - 0.17       | $m$-C=CPh       | 0.0529             | - 0.25       |

a) Measured in a MTHF glass matrix at 77 K; b) values given in cm$^{-1}$, accuracy > 0.0001 cm$^{-1}$; c) values given in $10^2$ cm$^{-1}$, $\Delta D = D_{1d} - D_X$.

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

![Graph](image1.png)  
Fig. 1: $\Delta D$ values of the monosubstituted 1 versus symmetrically disubstituted triplet diradicals $2$

![Graph](image2.png)  
Fig. 2: $D$ values of symmetrically disubstituted triplet diradicals $2$ versus $a_0$ hyperfine coupling constants of substituted cumyl monoradicals[5]
The \( \Delta D \) scale 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 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 spin sites \([3c]\).

\[
a_\beta = A + C \cdot \rho_\alpha \cdot \cos^2 \theta
\]  

(1)

\[
D = \left(3\mu_0 g^2 \rho^2 / 16\pi\right) \rho_A \rho_B / d^3
\]  

(2)

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

\[\text{Fig. 3: Experimental } D \text{ parameters of the triplet diradicals 2 versus the theoretical } \alpha \text{ spin density } (\rho_\alpha) \text{ of the cumyl monoradical fragments} \]

\( D \) 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° conformation (no delocalization between the radical site and the aryl moiety) and the 0° 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$_2$, p-NH$_2$ or m-NH$_2$, for which the angle dependence is exhibited in Fig. 4.

$$RSE = \Delta H_f(90°) - \Delta H_f(0°)$$  \hspace{1cm} (eq 3)

In Fig. 5 are displayed the correlations of the calculated RSE values with the experimental $D$ values of the triplet diradicals 2 and versus the calculated spin densities ($\rho_\alpha$).
The $\Delta D$ scale 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 $\sigma_{rad}$ scales for electronic substituent effects in radical reactions? To date, four chemical $\sigma_{rad}$ 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 $\sigma_{rad}$ values is mostly poor (Fig. 6); however, in the chemical $\sigma_{rad}$ 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 $\sigma_{rad}$ scales, a two-parameter Hammett analysis (eq 4) was performed for the Creary scale ($\sigma_{Creary}$), since this scale encompasses the largest set 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 ($\rho_{rad} = 1.00$ versus $\rho_{pol} = 0.41$).

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 ($\beta_0$), 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 $\sigma_{rad}$ values.
Fig. 7: Plots of $\Delta D$ against the Creary $\sigma_{rad}$ 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 $\sigma_{rad}$ 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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Literature