

The Importance of Spin Polarization in Electronic Substituent Effects of the Zero-Field EPR D Parameter in 1,3-Diarylcyclopentane-1,3-diyl Triplet Diradicals

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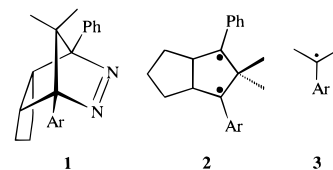
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Abstract: The zero-field-splitting D parameter of 11 *meta,para*-disubstituted 1,3-diarylcyclopentane-1,3-diyl triplet diradicals has been determined in a 2-MTHF glass matrix at 77 K by EPR spectroscopy. The experimental ΔD_{exp} value, conveniently defined as $D_{\text{H}} - D_{\text{X}}$, is a sensitive function of the delocalizing property of the X substituent on the phenyl ring. In contrast to the previously observed additivity for a large variety of *para* and *meta* substituents (cf. Adam, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Adv. Photochem.* **1998**, *24*, 205–254), such a simple relation no longer upholds for *meta,para* disubstitution. For the latter, the higher degree of spin delocalization is accounted for in terms of spin polarization and electronic field effects. For the first time also the increased spin density at the cumyl position caused by *meta* substituents has been satisfactorily explained by means of spin polarization. The spin density distribution in the cumyl radicals, computed by density functional theory (B3LYP/6-31g*), substantiate these experimental findings.

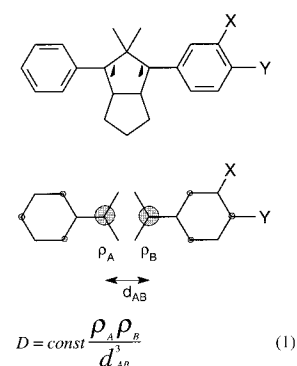
Introduction

A number of spectroscopic methods are available to assess the spin density at the radical centers of a triplet diradical. For example, by means of high-resolution EPR spectroscopy, from the hyperfine splitting of the half-field signals ($\Delta m_S = 2$) the spin density may be determined.¹ The disadvantage of this method is that a detailed study of the coupling pattern is necessary to get concrete information about the spin densities at the radical centers. However, due to the fact that the electron spin couples with all magnetically active neighboring nuclei (usually hydrogen atoms), the resulting complex coupling patterns are frequently difficult to interpret with certainty. In contrast, the zero-field-splitting parameter D of matrix-isolated triplet diradicals, readily and accurately measured by routine EPR spectroscopy at low temperature, obviates these limitations.

The zero-field-splitting parameter D of the localized 1,3-diaryl-substituted triplet diradicals **2**, provides important information on the steric and electronic properties of such high-spin systems.² While the E value, a measure of symmetry, is usually nearly zero ($E < 0.002 \text{ cm}^{-1}$) in cyclopentane-1,3-diyl triplet diradicals **2**, the D value (ca. 0.05 cm^{-1}) derives from the dipole–dipole interaction between the two unpaired spins and reflects the electronic nature of the diradical. The magnitude of this D parameter depends on the distance d_{AB} between the two



radical centers and the spin densities ρ_{A} and ρ_{B} (π -spin populations) at these radical sites (eq 1).³



While the distance d_{AB} in the triplet diradicals **2** is constant (ca. 238 pm),⁴ the spin density at the cumyl center (ρ_{B}) varies with the spin-delocalizing ability of the aryl group.⁵ Thus, the

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change of the *D* value, which for convenience is expressed by the ΔD value relative to phenyl (eq 2), is a sensitive probe for

$$\Delta D_X = 100(D_H - D_X) \quad (2)$$

the spin density at the cumyl position of the aryl group (ρ_B) and, therefore, a measure of electronic substituent effects on the spin distribution. Spin-localizing substituents lead to negative ΔD values and spin-delocalizing ones to positive ΔD values.

It has also been established by correlation between the experimental *D* values of the triplet diradicals **2** and the calculated benzylic spin densities of correspondingly substituted cumyl radicals **3** that the electronic substituent effects on the radical sites are comparable for both systems. Evidently, captodative stabilization and spin polarization between the two radical sites of the localized triplet diradical **2** do not significantly influence the spin densities.⁶ This important fact makes it possible to view the triplet diradical as a composite of two independent cumyl radicals. Therefore, the *D* parameter of the triplet diradicals **2** is a direct measure of the benzylic spin density of the cumyl radical.

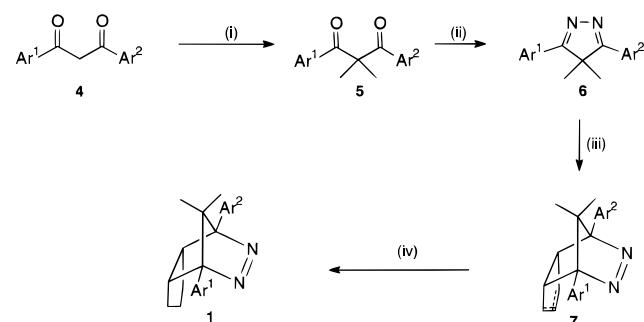
For the so-far studied triplet diradicals **2**, with few exceptions, all *para*-substituted triplet diradicals **2** have *D* values smaller than that of the unsubstituted parent system (positive ΔD values). In contrast, all *meta*-substituted triplet diradicals **2** have values higher than that of the parent system (negative ΔD values).⁷ This experimental observation has, to date, not been satisfactorily explained.^{8,11} For diradicals **2** with either two *meta* substituents on the same aryl ring or two *para* substituents on different aryl rings, the ΔD values are exactly twice those for diradicals with only one substituent. Thus, the additivity of the electronic substituent effects is strictly obeyed for a large set of *para* and *meta* substituents.

The aim of the present study is to explain why *meta* substituents increase the spin density at the cumyl site. For this purpose, ab initio DFT calculations on a selected set of *meta*- as well as *para*-monosubstituted and of *meta,para*-disubstituted cumyl radicals **3** have been made and the computed spin densities compared with the experimental *D* values for the corresponding triplet diradicals **2**. To assess whether the observed enhanced delocalizing effect (lack of additivity) of the *meta,para*-disubstituted triplet diradicals is caused by steric interactions between the adjacent substituents, derivatives with conformationally fixed cyclic substituents were examined.

Results

Syntheses. The substituted azoalkanes **1** served as precursors to the triplet diradicals **2** and were prepared in analogy to reported procedures (Scheme 1).¹² The derivative **5l** was directly obtained from 3,4-dicyanobenzoyl chloride and the silyl enol ether of isopropyl phenyl ketone under TiCl₄ catalysis. The

Scheme 1^a



^a Conditions: (i) CH₃I, NaH, toluene, ca. 80 °C, 2 d; (ii) N₂H₄·H₂O, CHCl₃, reflux, 16 h; (iii) cyclopentadiene, CF₃COOH (0.9 equiv), CH₂Cl₂, 0 °C, 2 d; (iv) H₂, Pd/C, AcOEt, 20 °C, 2 d.

unsaturated azoalkanes **7** were transformed into the saturated **1** to avoid regioisomers (Scheme 1).

EPR Spectroscopy. Photolysis of the azoalkanes **1** in 2-methyltetrahydrofuran (MTHF) glass matrix at 77 K with the 364-nm line of an argon ion laser afforded the persistent triplet diradicals **2**. Analysis of the *Z* signals in the EPR spectra (for a typical one cf. Figure 1 in ref 13) afforded the *D* parameters as half of the distance between the low- and the high-field peaks; the *E* parameters were expectedly very small (≤ 0.002 cm⁻¹). The EPR data are summarized in Table 1.

The experimental *D* values in Table 1 have been arranged in descending order, with the difluoro derivative **2b** the highest and dicyano **2l** the lowest. For convenience of comparison, the ΔD_{exp} values relative to the phenyl case as reference system are also given, which are calculated according to eq 2.⁷ A positive value signifies that the spin density at the cumyl radical site is decreased through delocalization by the aryl substituent relative to phenyl, while a negative value implies a higher spin density for the aryl versus phenyl groups. Except for **2b** and **2c** with negative ΔD_{exp} values, all others are positive. Thus, as expected, the cyano substituent (spin-accepting by conjugation) possesses a positive ΔD_{exp} value (cf. **2l**), while for the fluoro substituent (spin-donating by conjugation) the ΔD_{exp} value is negative (cf. **2b**). However, the methoxy substituent, which has been previously established as spin donor and should display a negative ΔD_{exp} value,^{3,5} falls out of the expected trend in that ΔD_{exp} is definitively positive (cf. **2k**). Thus, for the *meta,para*-dimethoxy derivative **2k**, the electronic effects on the *D* parameter are no longer additive, which is in sharp contrast to our previous findings.¹⁴ To assess quantitatively this discrepancy, we compared the actual ΔD_{exp} values with those expected from additivity, i.e., the ΔD_{add} values, which are defined by eq 3. The respective ΔD_{para} and ΔD_{meta} data are available from

$$\Delta D_{\text{add}} = \Delta D_{\text{meta}} + \Delta D_{\text{para}} \quad (3)$$

literature⁷ and are listed in Table 1, together with the ΔD_{add} values.

With the methoxy substituent as an example, let us illustrate the lack of additivity for the *meta,para* substitution pattern (substituents on the same phenyl ring) in derivative **2k** by comparing the ΔD_{exp} and ΔD_{add} values with the *meta,para*' substitution pattern (substituents on different phenyl rings) in **2a** (Figure 1). Clearly, additivity is obeyed for **2a** since ΔD_{exp} and ΔD_{add} are equal and, as expected for a spin donor, both are

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Table 1. Experimental D and ΔD Values of the Triplet Diradicals **2** and Calculated Cumyl Spin Densities ρ_{cum} of the Corresponding Monoradicals **3**

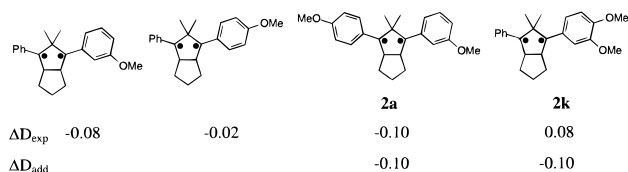
| 2 | Ar ¹ | D ^a | ΔD_{exp} ^b | ΔD_{add} ^c | ρ_{cum} ^d | ΔD_{para} ^e | ΔD_{meta} ^f |
|-----------------------|-----------------|-----------------|--------------------------------------|--------------------------------------|----------------------------------|---------------------------------------|---------------------------------------|
| b | | 5.09 | -0.03 | -0.14 | - | -0.08 | -0.06 |
| c | | 5.09 | -0.03 | -0.10 | 0.547 | | |
| d ^g | | 5.06 | 0.00 | 0.00 | 0.542 | | |
| e | | 5.05 | 0.01 | -0.03 | 0.539 | 0.01 | -0.04 |
| f | | 5.05 | 0.01 | -0.03 | 0.538 | | |
| g | | 5.04 | 0.02 | -0.03 | 0.540 | | |
| h | | 5.03 | 0.03 | 0.01 | 0.519 | 0.05 | -0.04 |
| i | | 5.03 | 0.03 | -0.06 | 0.530 | | |
| j | | 5.00 | 0.06 | -0.10 | 0.536 | | |
| k | | 4.98 | 0.08 | -0.10 | 0.528 | -0.02 | -0.08 |
| l | | 4.82 | 0.24 | 0.20 | 0.506 | 0.27 | -0.07 |

^a Experimental D values, divided by hc , are given in 10^{-2} cm^{-1} ; measured in a 2-MTHF matrix at 77 K, error $\pm 0.00002 \text{ cm}^{-1}$; $|E/hc| < 0.002 \text{ cm}^{-1}$. ^b Calculated according to $\Delta D_{\text{exp}} = 100(D_{\text{H}} - D_{\text{X}})$, with a reference D_{H} value of 0.0506 cm^{-1} for the unsubstituted diradical. ^c Theoretical ΔD values calculated by $\Delta D_{\text{add}} = \Delta D_{\text{para}} + \Delta D_{\text{meta}}$. ^d PM3-calculated spin densities defined as the square of the SOMO p_z coefficient of the cumyl carbon in the monoradical **3**. ^e ΔD value of the diradical with only a *para* substituent on one aromatic ring.⁶ ^f ΔD value of the diradical with only a *meta* substituent on one aromatic ring.⁶ ^g Reference system.

negative. In contrast, a large deviation between ΔD_{exp} and ΔD_{add} is observed for **2k**, even the signs are opposite. Thus, the methoxy substituents in the *meta,para*-disubstituted **2k** act as spin acceptors (positive ΔD_{exp}). Since the two methoxy groups are *ortho* to one another, steric effects between the methyl groups might twist the oxygen lone pairs out of conjugation with the phenyl π system and thereby reduce the spin-donating effect. That such a conformational influence cannot be the cause for the loss of additivity is shown by the cyclic derivative **2j**, which despite its planarity also exhibits a large deviation between the ΔD_{exp} and ΔD_{add} values. Like the *meta,para*-dimethoxy derivative **2k**, also the acetal functionality in **2j** acts as spin acceptor.

Although this discrepancy is most pronounced for the methoxy substituent, all *meta,para*-disubstituted derivatives of the triplet diradical **2** in Table 1 disobey additivity, namely the F (**2b**), Me (**2e**), Cl (**2h**), and CN (**2l**) derivatives. Therefore, the lack of additivity is a general phenomenon for *meta,para* disubstitution in the same phenyl ring and requires rationalization. Our theoretical analysis (cf. Discussion) discloses that *spin-polarization* and electronic field effects are responsible.

Spin-Density Dependence of the D Values. As eq 1 shows, a direct dependence exists between the experimental D parameter of the localized triplet diradicals **2** and **3** and the theoretically accessible spin densities ρ_{A} and ρ_{B} at the radical termini A and B, provided the distance d_{AB} is constant. The latter requisite applies for the localized diradicals under study here, since $d_{\text{AB}} = 2.38 \text{ \AA}$ of the reference system **2d** is the same for all other derivatives **2**.

**Figure 1.** Dependence of the ΔD value on the substitution pattern.

The spin densities at the cumyl position of the corresponding *meta,para*-disubstituted radicals **3** were calculated by the semiempirical PM3 method and by ab initio (B3LYP) density functional theory (DFT), the latter only for a representative set. For the PM3¹⁵ method, the geometry optimization of the model cumyl radicals **3** was made by using the annihilated UHF wave function.¹⁶ The cumyl spin densities ρ_{cum} ⁷ were then computed by a single-point CI calculation.¹⁷ In the case of the DFT calculations, the geometry was preoptimized for UHF wave functions. The spin densities were determined by B3LYP calculations with the 6-31G* basis set.¹⁸ In this case, again only the spin in the z direction was considered in the computation of the total atomic spin.

Both procedures gave results for the cumyl spin densities (ρ_{cum}) which are in reasonable agreement with the experimental values derived from the hyperfine coupling constants.^{17,19} For the cumyl radical **3d**, the ρ_{cum} values are 0.542 (PM3) and 0.627 (B3LYP), compared to the experimental value of 0.587 (within 6–8%). The B3LYP-calculated spin densities at the *ortho* (ρ_{ortho}) and *para* (ρ_{para}) positions of the cumyl radical **3d** are 0.178 and 0.194, compared to the corresponding experimental values 0.204 and 0.241. The respective PM3 values of 0.121 and 0.123 display a less satisfactory correspondence compared to the B3LYP results. In the PM3 case, the relative values for the *ortho* and *para* positions are nearly equal, while the experimental as well as the B3LYP results show a significantly higher spin density in the *para* position than in the *ortho* position.

As shown in Figure 2, there is a good linear dependence ($|D/hc| \times 100 = 18.2\rho_{\text{cum}}^2 - 0.226$; $r^2 = 0.951$) between the D parameter of the symmetrically substituted triplet diradical **2** and the square of the calculated cumyl spin densities ρ_{cum} of the corresponding monoradicals **3**. The good correlation confirms once more that the D value is proportional to the cumyl spin density and justifies, therefore, the use of the D value for the triplet diradicals **2** to assess the spin-density distribution in the corresponding cumyl monoradicals **3**.

Radical Stabilization Energies. The radical stabilization energy (RSE), a theoretical parameter which provides a quantitative measure of the delocalization of the unpaired electron in the cumyl radical, reflects the degree of stabilization

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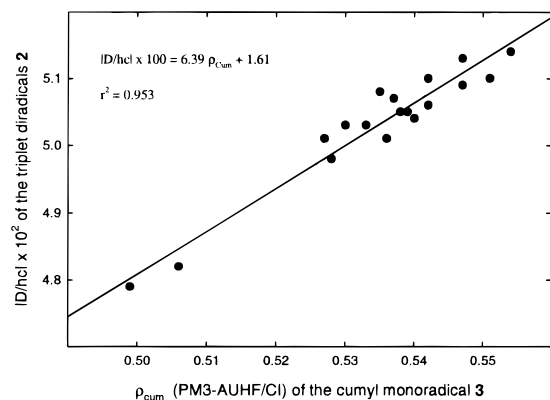


Figure 2. Experimental *D* parameter (cm^{-1}) of the substituted triplet diradicals **2** versus calculated spin density of the corresponding monoradicals **3**.

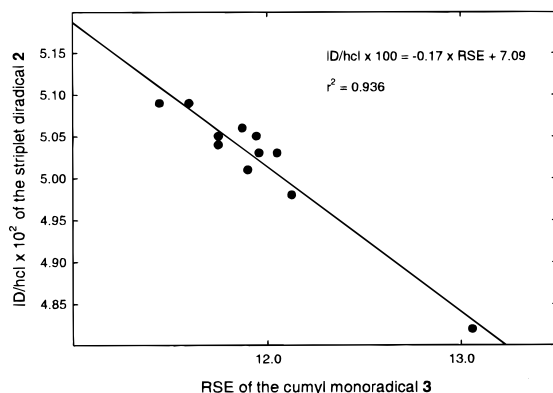


Figure 3. Experimental *D* parameter (cm^{-1}) of the substituted triplet diradicals **2** versus the calculated RSE values (kcal/mol) of the corresponding monoradicals **3**.

compared to the isopropyl radical as reference. The RSE of a cumyl radical may be estimated according to eq 4, which

$$\text{RSE} = \Delta H_f(90^\circ) - \Delta H_f(0^\circ) \quad (4)$$

represents the barrier of rotation around the C–C bond between the radical center and the aromatic ring as the difference between the energy of the 90° (no spin delocalization) and the 0° (maximal spin delocalization) conformers.^{17,19,20} The RSE values were computed on a selected set of substituents (the full range of substituent effects was spanned) by the PM3 method as described above for the spin-density calculations of the cumyl radical.^{16,18} As shown in Figure 3, again a good linear dependence was found for the calculated RSE values of the cumyl monoradical **3** and the experimental *D* parameters of the corresponding triplet diradicals **2** ($|D/hc| \times 100 = -4.42(\text{RSE}) + 8.51$; $r^2 = 0.937$). In agreement with earlier results,¹⁷ the semiempirically (PM3) calculated RSE values afford rotation barriers which are, by a factor of 3–4, smaller than the experimental ones. Nevertheless, these results demonstrate that the relative trend in the electronic substituent effects on the spin density (ρ_{cum}) and the radical stabilization energy (RSE) for the cumyl radical **3** are well accounted for by the experimental *D* parameters of the corresponding triplet diradicals **2**.

Discussion

Spin Polarization in Radicals. Examination of the spin distribution in the allyl radical by Hückel theory shows that the unpaired electron is only localized on the two outer carbon

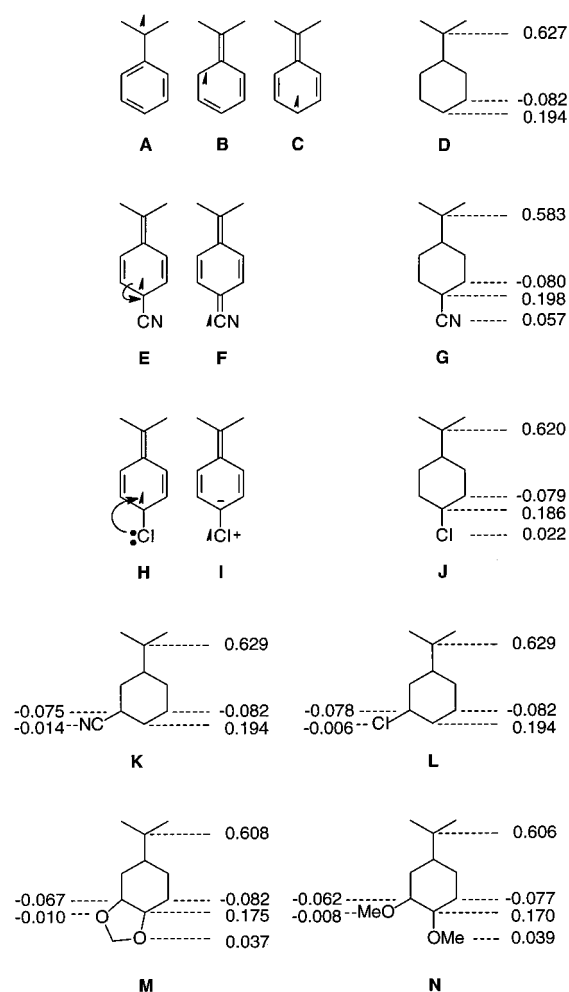


Figure 4. DFT-computed spin-density (ρ) distributions in cumyl radicals; positive ρ values represent α spin and negative ones represent β spin.

atoms, while on the central one there resides no spin. This is due to the fact that the spin-bearing singly occupied molecular orbital (SOMO) has a node at this position and its coefficients at the outer carbon atoms are exactly 0.707. A more detailed examination reveals an interaction between the unpaired electron in the SOMO and the two highest occupied molecular orbital (HOMO) electrons, a phenomenon known as *spin polarization*.²¹ In view of the Pauli exclusion principle, localization of α spin at the outer carbon atoms in the HOMO is energetically favored but is compensated by location of β spin at the central carbon atom. As a result of this polarization, the α spin at the outer carbon atoms becomes higher than predicted by simple Hückel theory, and at the central carbon atom a β spin is induced. This spin at the central position may be measured by EPR spectroscopy through the hyperfine coupling constant (hfc) for the hydrogen atom connected to the central atom.

Similarly, in the simple mesomeric picture for a cumyl radical, the unpaired electron (α spin) may only be delocalized to the *ortho* and *para* positions of the aromatic ring, while at the *ipso* and *meta* positions there should be no spin (**A–C** in Figure 4). EPR experiments reveal, however, that at the *meta* position again a β spin is induced by spin polarization. The resulting α - and β -spin densities may be calculated by DFT; by convention, the

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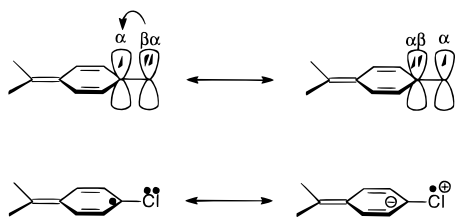


Figure 5. α -Spin delocalization by β -spin donation of an $S_{\beta}D$ substituent in the *para* position.

β spin takes negative values and the α spin positive values. As one can see from the spin-density calculation on the cumyl radical (structure **D** in Figure 4), the spin at the *para* position is α oriented, and that at the *meta* position is β oriented. What are the consequences of this spin polarization for different substituents and substitution patterns?

Substituent Effects. Previously⁷ we have classified the electronic effects of substituents on an unpaired electron (spin) into two categories, namely spin acceptors (SA) and spin donors (SD). Spin acceptors (e.g., cyano) are typically unsaturated groups and delocalize the unpaired electron into unoccupied π -type orbitals of the substituent (structures **E** and **F** in Figure 4). Spin donors (e.g., chloro) contain lone pairs and delocalize an unpaired electron by donation of an electron from the lone pair of the substituent (structures **H** and **I** and Figure 4). Although the net effect is spin localization at the cyano and chloro substituents, the mechanisms are fundamentally different. To make this clear, we must consider spin orientation, i.e., α spin (spin up) versus β spin (spin down). Let us assign α spin at the cumyl site, as shown in structure **A** (Figure 4). The SA-type *para*-cyano substituent accepts this α spin by delocalization, as displayed by the quinoid structure **F**. In contrast, the SD-type *para*-chloro substituent acquires α spin by donation of an electron with β spin from its lone pair to afford the zwitterionic radical structure **I**. This is portrayed more explicitly in Figure 5, in which the spin orientations of the involved electrons are shown. Through the advent of spin polarization, a position in the aromatic ring of the cumyl radical may bear α spin (*ortho* and *para* positions) or β spin (*meta* and *ipso* positions). Consequently, and as will become evident when we analyze separately the electronic effects of *para* and *meta* substituents, it is necessary to extend our SA/SD classification by taking account of α/β -spin orientation. Thus, we redefine⁷ the following four types of substituents: (a) $S_{\alpha}A$ accepts α spin from the aromatic ring, (b) $S_{\beta}A$ accepts β spin from the aromatic ring, (c) $S_{\alpha}D$ donates α spin to the aromatic ring, and (d) $S_{\beta}D$ donates β spin to the aromatic ring.

It should be emphasized that, in contrast to the differentiation of substituents as spin donors (SD) and spin acceptors (SA),⁷ which is an inherent electronic feature of the substituent, the distinction in terms of α and β spins is not related to the electronic nature of the substituent but is imposed by spin polarization, which induces β spin at the *meta* position through concentration of α spin at the *para* and *ortho* sites. Of course, the net spin (the sum of α and β spins) must be unity for the radical.

Para Substitution. With few exceptions, all *para* substituents reduce the cumyl spin density^{7,9–11} relative to the unsubstituted parent system **3d** through delocalization of α spin from the cumyl to the *para* position, as revealed by structure **C** (Figure 4). If the *para* position bears an $S_{\alpha}A$ substituent, this α spin is further delocalized through the quinoid structure **F** (Figure 4) such that α spin is localized on the substituent. This α -spin delocalization by the $S_{\alpha}A$ substituent is confirmed by ab initio

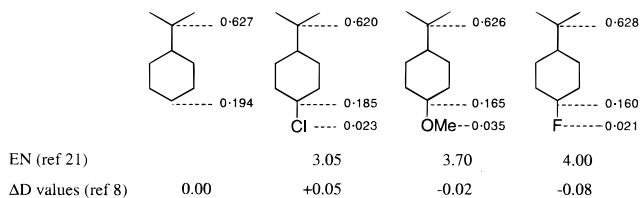


Figure 6. Spin-density enhancement at the cumyl radical site by the electronegative (EN) *para* substituents.

DFT calculations (structure **G** in Figure 4), which clearly show a lower α -spin density at the cumyl position compared to the parent system (structure **D**), while the *para*-cyano substituent has acquired α spin. Consequently, the α spin at the cumyl site is delocalized into the aromatic ring more effectively by the $S_{\alpha}A$ substituent than in the unsubstituted cumyl radical, as evidenced experimentally by the D value.

In contrast, a $S_{\beta}D$ substituent, e.g., chloro, delocalizes the α spin from the *para* position of the cumyl radical by donating β spin from the π -aligned nonbonding lone pair into the aromatic ring. The zwitterionic mesomeric structure **I** (Figure 4) is formed with a negative charge in the aromatic ring and a positive charge as well as α spin (Figure 5) on the substituent. The DFT calculations corroborate this effect, since in structure **J** (Figure 4) the α spin at the cumyl position is lowered compared to the parent system (structure **D**), while the chloro substituent now bears α spin. Thus, the $S_{\beta}D$ -type substituent also acts as an α -spin acceptor, but by β -spin donation from its lone pair, and the cumyl spin density is lowered.

Like chloro, also the fluoro atom in the *para* position should act as an $S_{\beta}D$ substituent and reduce the α spin in the cumyl position by β -spin donation. Experimentally, this was not observed, as displayed by the ΔD_{para} value of -0.08 for the *para*-fluoro-substituted diradical; in fact, the α -spin density is enhanced at the cumyl position. Similarly, also for the *para*-acetoxy ($\Delta D_{para} = -0.05$) and *para*-methoxy ($\Delta D_{para} = -0.02$) functionalities, more α spin resides at the cumyl site, but the enhancement is less pronounced than for the *para*-fluoro substituent. These highly electronegative groups appear to act as α -spin donors ($S_{\alpha}D$), but they are destined to serve as β -spin donors ($S_{\beta}D$) because at the *para* position, to which they are attached, resides α spin through the usual benzyl-type delocalization. Therefore, an alternative mechanism must operate for the *para*-fluoro substituent, which overcompensates its $S_{\beta}D$ nature to enhance the α -spin density at the cumyl site. The high electronegativity of the fluorine element is evidently responsible for this effective α -spin enhancement. The strong inductive effect of the *para*-fluoro substituent lowers substantially the energy of the $2p_z$ orbital at the *para* carbon atom and thereby perturbs the efficacy of spin delocalization by the aromatic π system.^{11b}

Computations substantiate this electronegativity effect, as exhibited in Figure 6. Given are the α -spin densities at the cumyl and *para* positions and at the *para* substituent, together with the electronegativities²² and the ΔD values for the parent cumyl radical and the *para*-substituted derivatives Cl, OMe, and F. For the most electronegative *para*-F (0.160), the α -spin density in the z direction at the *para* position is substantially lower (less effective α -spin delocalization) than for the parent cumyl radical (0.194), while for the less electronegative *para*-OMe (0.165) and *para*-Cl (0.185) groups it falls in between those of *para*-F and the parent. Thus, on account of the less effective α -spin

(22) Boyd, J. R.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182–4186.

delocalization for the *para*-fluorophenyl versus the phenyl group, more α spin is localized at the cumyl radical center, and correspondingly the spin density at the cumyl site is enhanced. Because the effective enhancement of α spin at the cumyl position by this substituent is very small (about the 1% compared to the parent system), the computed spin density at the cumyl position shows no change.

In order not to mistake this spin-density enhancement with the α -spin-donation ($S_{\alpha}D$) mechanism, the *para*-fluoro substituent is designated as an α -spin enhancer ($S_{\alpha}E$), for which the enhancement is caused by spin localization due to its high electronegativity rather than spin delocalization. The α -spin localization of the $S_{\alpha}E$ mechanism overrides the α -spin delocalization of the $S_{\beta}D$ mechanism for the *para*-fluoro substituent, and, thus, the net effect is a higher spin density at the cumyl site, as experimentally confirmed by the negative ΔD value (-0.08). For the less electronegative *para*-methoxy group, the $S_{\alpha}E$ (α -spin localization through the electronegativity effect) and the $S_{\beta}D$ (α -spin delocalization through β -spin donation) mechanisms are at balance, such that the ΔD value (-0.02) is nearly zero. The $S_{\beta}D$ mechanism dominates for the *para*-chloro substituent, and the ΔD value ($+0.05$) is positive, typical for α -spin delocalization through β -spin donation by such a *para* substituent.

Meta Substitution. In contrast to *para* substituents, *meta* ones all raise the benzylic spin density. It shall become evident that spin polarization is the reason for this *meta* effect, and this provides for the first time an adequate rationale for this empirical fact.^{7,8,11} As mentioned before, the α spins in the aromatic *ortho* and *para* positions of a cumyl radical induce a β spin in the *meta* position through spin polarization, manifested by the negative spin density at the *meta* site in structure **D** (Figure 4). Thus, substituents at the *meta* position reduce this β spin by the same mechanisms responsible for the reduction of an α spin in the *para* position.

A $S_{\beta}A$ -type substituent in the *meta* position reduces this β spin by delocalization onto the spin-accepting group, e.g., the *meta*-CN substituent in structure **K** (Figure 4). In contrast, an $S_{\alpha}D$ -type substituent, e.g., *meta*-Cl, delocalizes the β spin at the *meta* position by donation of α spin from its π -aligned nonbonding lone pair and thereby accumulates β spin, as evidenced in structure **L**. While the spin-delocalization mechanisms are the same for the *meta* and *para* positions, the effects on the spin density at the cumyl site are opposite: for *para* substituents, both $S_{\alpha}A$ and $S_{\beta}D$, the α -spin density at the cumyl position is decreased, while *meta* substituents lower the β -spin density at the cumyl position. Since the net spin density (the only experimental quantity measurable by EPR spectroscopy through the hyperfine coupling constants) is the difference of the α - and β -spin densities, effectively the α -spin density at the cumyl position is increased by *meta* substitution.

To clarify this important point, we shall consider the theoretical (ab initio) spin densities (Figure 4).²³ For the parent cumyl radical (structure **D** in Figure 4), the spin density at the cumyl position is $+0.627$ (α spin), and at the *meta* site it is -0.082 (β spin) through spin polarization. If a *meta* substituent carries some β spin, the α spin in the remaining cumyl radical fragment must become larger to offset this spin localization on the substituent. As result of the increased α spin in the remaining cumyl fragment, the spin density at the cumyl position must also be increased relative to the parent system. This expectation

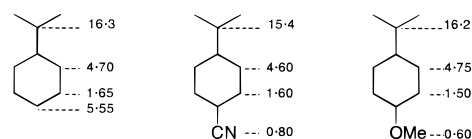


Figure 7. EPR hyperfine coupling constants of cumyl radicals (ref 18).

is nicely corroborated by the DFT-computed spin densities for the $S_{\beta}A$ -type *meta*-CN (structure **K**) and the $S_{\alpha}D$ -type *meta*-Cl (structure **L**) substituents in Figure 4. Both *meta* substituents carry β spin (-0.014 for *meta*-CN and -0.006 for *meta*-Cl), while the α spin at the cumyl positions is slightly increased (for both $+0.629$) versus the parent system ($+0.627$). This change of spin density at the cumyl position is small but expected since the D value of the *meta*-Cl substituent is increased by only 0.8%. Also, the β spin in the *meta* position itself is lowered because of delocalization onto the substituent (i.e., -0.075 and -0.078 versus -0.082 for the parent system). Thus, these *meta* substituents both act effectively as α spin donors and increase the net cumyl spin density as a consequence of spin polarization.

The *meta* effects are considerably smaller compared to the *para* ones, but fortunately, through the high sensitivity of the D parameter, even such small electronic perturbations are accurately measured quantitatively for the localized triplet 1,3-diradicals under scrutiny. The reason for the small *meta* effects resides in the fact that the spin density in the *meta* position is significantly smaller than in the *para* one. For example, the DFT spin densities of the parent cumyl radical are 0.194 versus 0.082 in structure **D** (Figure 4), i.e., at the *para* site more than twice that at the *meta* one. Thus, a *para* substituent changes the spin density at the cumyl site more effectively than a *meta* one.

Meta,para-Disubstitution. We have seen that *meta* substituents normally increase and *para* substituents decrease the spin density at the cumyl position. For *meta,para*-disubstituted derivatives, without any further interaction between the two substituents, their electronic effects should be additive. Thus, the ΔD_{add} value that results from simple addition of the separate *meta* and *para* substituents should be equal to the ΔD_{exp} of the *meta,para*-disubstituted triplet diradical. This additivity is found for triplet 1,3-diradicals **2** with two *meta* substituents on the same aromatic ring,⁷ as well as for the derivative **2a** with one ring *meta* substituted and the other one *para* substituted (Figure 1).

As we have already mentioned (Table 1), for triplet diradicals with two adjacent substituents in the *meta* and *para* positions, there is no additivity; for all cases, ΔD_{exp} is more positive than the expected ΔD_{add} . Thus, the juxtaposition of a pair of *meta* and *para* substituents in a cumyl radical provides better delocalization by the aryl moiety and reduces the cumyl spin density compared to the value expected from the additivity of their separate electronic effects.

To understand this anomaly, the DFT spin densities were calculated at the *meta* position of *para*-substituted cumyl radicals (**G** and **J**, Figure 4). Comparison with the parent system **D** reveals that the spin densities of the *para*-substituted derivatives are slightly decreased. While one might argue that this small decrease is insignificant, the same small trend is also seen for the EPR hyperfine coupling constants¹⁹ (hfc) of the *para*-substituted cumyl radicals. Thus, the *para* substituent decreases the coupling constant in the *meta* position (Figure 7), and since the coupling constant depends directly on the spin density, less β spin resides at the *meta* position, as confirmed by the DFT calculations. Since substituents at the *meta* position, which

(23) A quantitative account of the *meta* effect by ab initio calculation is not feasible because this effect is too small, such that the increase in the spin density (maximally 1.5% for the substituents under investigation here) at the cumyl position is within the error of the calculations.

carries β spin through spin polarization, may delocalize this spin either by direct acceptance of β spin or by donation of α spin, the strength of this delocalization depends on the spin density located at the carbon atom to which the substituent is connected. DFT calculations and hfc measurements show that, in the *para*-substituted systems, the β -spin density in the *meta* position is reduced and, hence, also the propensity of the *meta* substituent to accept β spin or donate α spin diminishes. As a consequence, the electronic effects of the substituents are no longer additive, and the spin density at the cumyl position is lower compared to the value expected for simple substituent additivity. Consequently, ΔD_{exp} is more positive than the corresponding ΔD_{add} value, and the *meta,para*-disubstituted derivatives delocalize spin better than the parent system **2d**.

Let us illustrate this lack of additivity for the acceptor-substituted *meta,para*-dicyano case with an $S_{\alpha A}$ -type substituent in the *para* position and an $S_{\beta A}$ -type one in the *meta* position. For this triplet diradical **2l**, both positive ΔD values ($\Delta D_{\text{exp}} = 0.24$ versus $\Delta D_{\text{add}} = 0.20$) clearly show that the cumyl spin density is reduced compared to the parent system **2d**, and, thus, the spin of the *meta,para*-dicyano derivative **2l** is more effectively delocalized; however, the more positive ΔD_{exp} (0.24) value than ΔD_{add} (0.20) displays better delocalization than expected from additivity. This is due to the reduced β -spin density at the *meta* position (less effective spin polarization) caused by the *para* substituent ($\Delta D_{\text{para}} = 0.27$), which diminishes the counteracting spin-localizing effect of the *meta*-cyano substituent ($\Delta D_{\text{meta}} = -0.07$). The net effect is that *meta,para*-dicyano substitution provides better spin delocalization than expected, but of course not as much as *para*-cyano substitution alone. Thus, the spin-localizing nature of the *meta*-cyano group still operates in the *meta,para*-dicyano derivative and counteracts the spin delocalization by the *para*-cyano group, but not as effectively as for the two separate cases!

In contrast, for the *meta,para*-dimethoxy triplet diradical **2k**, which contains a *para*- $S_{\alpha E}$ substituent and a *meta*- $S_{\alpha D}$ substituent, the spin-localizing effect in **2k** is not only diminished, but this aryl group is converted into an spin-delocalizing one. Thus, ΔD_{exp} (0.08) is not only higher than ΔD_{add} (-0.10) but also significantly higher than ΔD_{para} (-0.02) of the separate *para* substituent. Indeed, its appreciable positive ΔD_{exp} value means that, while the separate *para*-methoxy ($\Delta D_{\text{para}} = -0.02$) and *meta*-methoxy ($\Delta D_{\text{meta}} = -0.08$) substituents are spin localizing compared to the parent system, in combination they delocalize spin from the cumyl site. This unusual effect cannot be explained in terms of spin polarization alone, i.e., reduction of β -spin density in the *meta* position. For a spin-donating methoxy substituent to delocalize α spin from the cumyl radical site by β -spin donation (Figure 5), α spin must reside at the position at which the substituent is attached. For a *para* substituent, direct conjugation provides for this necessity through the quinoid resonance structure; however, for a *meta* substituent, the *meta* position acquires β -spin density through spin polarization by the α spin at the *para* position. Irrespective of the nature of the substituent at the *para* position, some α spin must reside at this site, and, thus, some β spin accumulates at the *meta* position but no α spin. Hence, there is no way for a *meta* substituent to delocalize α spin and thereby reduce the α -spin density at the cumyl radical site.

Since spin polarization does not account for the observed spin delocalization by the *meta-para* combination of two spin-donating methoxy groups, what electronic effects are responsible?

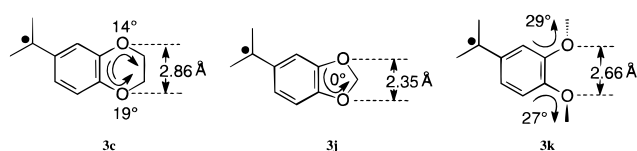


Figure 8. Calculated dihedral angles (the sense is defined by the curved arrows) and inter-oxygen distances of cumyl radicals **3c**, **3j**, and **3k**.

Examination of the series of the related triplet diradicals **2c**, **2j**, and **2k** provides a clue. In all three cases, the *meta* and *para* positions are substituted with oxygen atoms, and their ΔD_{exp} values should be similar; however, as the data in Table 1 reveal, ΔD_{exp} for **2c** is negative (-0.03), but it is positive for both **2j** (0.06) and **2k** (0.08). Clearly, of these *meta,para*-disubstituted derivatives, only **2c** acts as a spin donor, but its efficacy is lower compared to the monosubstituted *meta*-methoxy case. This is certainly a consequence of the reduced spin polarization induced by the *para*-methoxy group. For the *meta,para*-disubstituted **2j** and **2k** derivatives, in which the aryl groups operate as spin acceptors, evidently the zwitterionic resonance structure promotes spin delocalization (Figure 5). Through the charge polarization in this zwitterionic structure, negative charge accumulates in the aromatic ring, and positive charge accumulates on the *para* oxygen substituent. We propose that the positive charge on the *para* oxygen atom is stabilized by interaction with the lone pair of the adjacent *meta* substituent through the electronic field effect.²⁴ This field effect depends on the distance between the two oxygen atoms and the conformational orientation (dihedral angle) of the adjacent oxygen lone pairs, which are given in Figure 8 for the three cumyl radicals **3c**, **3j**, and **3k**. The largest distance between the two oxygen atoms is observed in derivative **3c**, for which also conformational constraint aligns poorly the lone pair of the *meta* oxygen atom. Consequently, charge stabilization is weak, and in this *meta,para*-disubstituted system the oxygen functionalities display net spin donation (less delocalization), as evidenced by the negative ΔD_{exp} value (-0.03) of **2c**, although its efficacy is decreased through the reduced spin polarization. In contrast, for the conformationally planar derivative **3j**, the inter-oxygen distance is significantly smaller, and effective stabilization of the positively charged *para* oxygen atom by the field effect of the adjacent *meta* lone pair enhances the contribution of the zwitterionic structure. This occurs to such an extent that the aryl ring promotes spin delocalization and the cumyl spin density is decreased, as evidenced by the positive ΔD_{exp} value of **2j** ($+0.06$). In the *meta,para*-dimethoxy derivative **2k** ($\Delta D_{\text{exp}} = 0.08$), spin delocalization is still more pronounced, although the distance between the oxygen functionalities in **2k** is larger than in **2j**. For the conformationally flexible methoxy group, the lone pair of the *meta* oxygen atom may be favorably aligned to point toward the positively charged *para* oxygen and thereby stabilize better the zwitterionic structure. For the **2k** and **2j** derivatives, this electronic stabilization of the zwitterionic structure outweighs the spin-donating effect of the *meta* oxygen functionalities, and spin delocalization into the *meta,para*-disubstituted aromatic ring is considerably better than for the parent phenyl group. In terms of the counteracting $S_{\beta D}$ (α -spin delocalization through β -spin donation) and $S_{\alpha E}$ (α -spin localization through the electronegativity effect) mechanisms for the *para*-methoxy substituent, which we have seen to be nearly equal in the absence of the *meta*-methoxy substituent, in the presence of the *meta*-methoxy groups the β -spin-donating effect (lowering of the cumyl spin density) now dominates because of the charge stabilization through the electronic field effect.

(24) Barkhash, V. A. *Top. Curr. Chem.* **1984**, 116/117, 1–265.

Also for the other *meta,para*-disubstituted derivatives, non-additivity of the electronic substituent effects is observed. For the difluoro triplet diradical **2b** and the mixed alkyl-oxygen-substituted one **2i**, the spin density is diminished compared to the *para*-substituted reference systems. The spin-localizing effect of the *meta* substituent is converted into a delocalizing one ($\Delta D_{\text{exp}} > \Delta D_{\text{para}}$), as described above for the dimethoxy case **2k**. In contrast, for the dichloro triplet diradical **2h**, the spin-localizing effect of the *meta* substituent is only diminished ($\Delta D_{\text{exp}} < \Delta D_{\text{para}}$), as described for the dicyano case **2l**. For the dialkyl-substituted derivatives **2e–g**, expectedly the *meta* substituent exerts only a small effect, if any, on the D value ($\Delta D_{\text{exp}} \approx \Delta D_{\text{para}}$); alkyl groups lack lone pairs and π bonds and interact only weakly with the spin.

In summary, donation and acceptance of spin by a substituent depends on the spin orientation (α and β) at the aromatic carbon atom to which the substituent is connected. In the case of a *para* substituent, the α spin at the cumyl site is decreased and that at the substituent is increased through spin delocalization, as confirmed by the positive ΔD value. For *meta* substituents, the opposite effect is observed in that α spin is increased at the cumyl site through β -spin delocalization (spin polarization), as evidenced by the negative ΔD value. For the combination of *meta* and *para* substituents on one aryl ring, electronic interac-

tions between the substituents come into play which are responsible for the breakdown of the additivity of their electronic effect. Thus, reduction of the β -spin density (lower spin polarization) at the *meta* position by the *para* substituent diminishes the spin-localizing effect of the *meta* substituent. For spin-enhancing substituents such as the methoxy group, additionally electronic field effects operate which stabilize zwitterionic resonance structures, and such *meta,para*-disubstituted systems promote spin delocalization and, thus, more effective stabilization of the cumyl radical.

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Supporting Information Available: Synthetic and computational details, characteristic spectral data of the 1,3-propanediones **4**, 2,2-dimethyl-1,3-propanediones **5**, 4,4-dimethyl-4*H*-pyrazoles **6**, and the azoalkanes **1** and **7** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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