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Additivity of the Electronic *Meta*-Substituent Effect in 3,5-Disubstituted Cumyl Radicals Assessed by the EPR *D* Parameter of 1,3-Arylcyclopentane-1,3-diyl Triplet Diradicals

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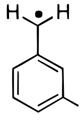
The *D* parameter (EPR zero-field splitting) of the 3,3′,5,5′-tetrasubstituted triplet diradicals **6** (X = X′ = H, NO_2, CH_3, OAc, OCH_3, NH_2, and OH) were determined in a MTHF matrix at 77 K and serves as a spectroscopic tool for the determination of electronic substituent effects in multiply-substituted benzyl-type monoradicals through its spin density dependence. The linear correlation ($m = 2.00 \pm 0.01$, $r^2 = 0.974$) of the experimental *D* values of these *meta*-disubstituted triplet diradicals **6** *versus* the 3,3′-disubstituted triplet diradicals **5** demonstrates the *additivity* of the electronic *meta*-substituent effect in the corresponding 3,5-disubstituted cumyl monoradicals **4** and is corroborated by theoretical (PM3-AUHF) spin density calculations for the latter. Thus, the combined use of the experimental *D* parameter and semiempirically calculated α spin density has provided for the first time the unambiguous demonstration of the *additivity* of electronic effects exerted by *meta*-substituents in the cumyl monoradicals **4**.

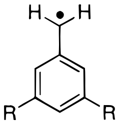
Introduction

Persistent localized triplet 1,3-diradicals of the cyclopentane-1,3-diyl-type are conveniently prepared under matrix isolation at cryogenic temperatures (4−77 K), and their electronic and structural properties are accessible through the EPR zero-field-splitting parameters *D* and *E*,[1] which derive from the dipole−dipole interaction between the two uncoupled spins.[2] The magnitude of the *D* parameter in localized triplet 1,3-diradicals such as **5** and **6** depends on the interspin distance d_{AB} and the α spin densities ρ_A and ρ_B at the radical sites A and B (eq 1), and both dependences have recently been confirmed experimentally and theoretically.[3]

$$D = \frac{3\mu_0 g^2 \mu_B^2}{16\pi}\left(\frac{\rho_A \rho_B}{d_{AB}{}^3}\right) \qquad (1)$$

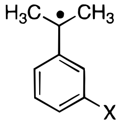


1



2

R = H, CF_3, OCH_3,
F, ^{t}Bu, Cl, CH_3



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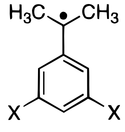
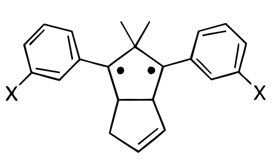


4

X = H, NO_2, CH_3, OAc,
OCH_3, NH_2, OH



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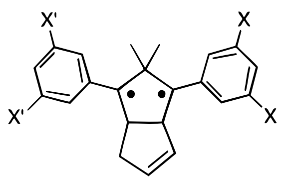

6

Such localized 1,3-diaryl-substituted cyclopentane-1,3-diyl triplet diradicals can be described as two geometrically fixed but independent cumyl monoradicals. Thus, at constant d_{AB}, the *D* parameter is a sensitive probe for electronic substituent effects through the α spin density dependence[3b] and the data for the symmetrically *para*- and *meta*-substituted 1,3-diarylcyclopentane-1,3-diyl triplet diradicals **5** have formed the basis for the spectroscopic Δ*D* scale (eq 2).[3a,c,d] In this context, we have

$$\Delta D = (D_X - D_H)100 \qquad (2)$$

shown that *meta*-substitution in the cumyl radicals **3** *destabilizes* the radical at the α site by increased spin localization relative to the parent radical **3** (X = H), which is expressed in the negative Δ*D* values for all *meta*-substituents. This electronic peculiarity, which has been a conflicting point in all other σ_{rad} scales,[4−8] was corroborated for the first time by semiempirical MO calculations and by a satisfactory correlation with the Swain−Lupton resonance parameter *R*.[3d]

In contrast, only little attention has been focused on the electronic effects caused by *meta*-disubstitution in the monoradicals **2** and **4**, albeit for ionic reactions it is the consensus of opinion that electronic substituent effects are additive, as diagnosed by the Hammett equation.[9]

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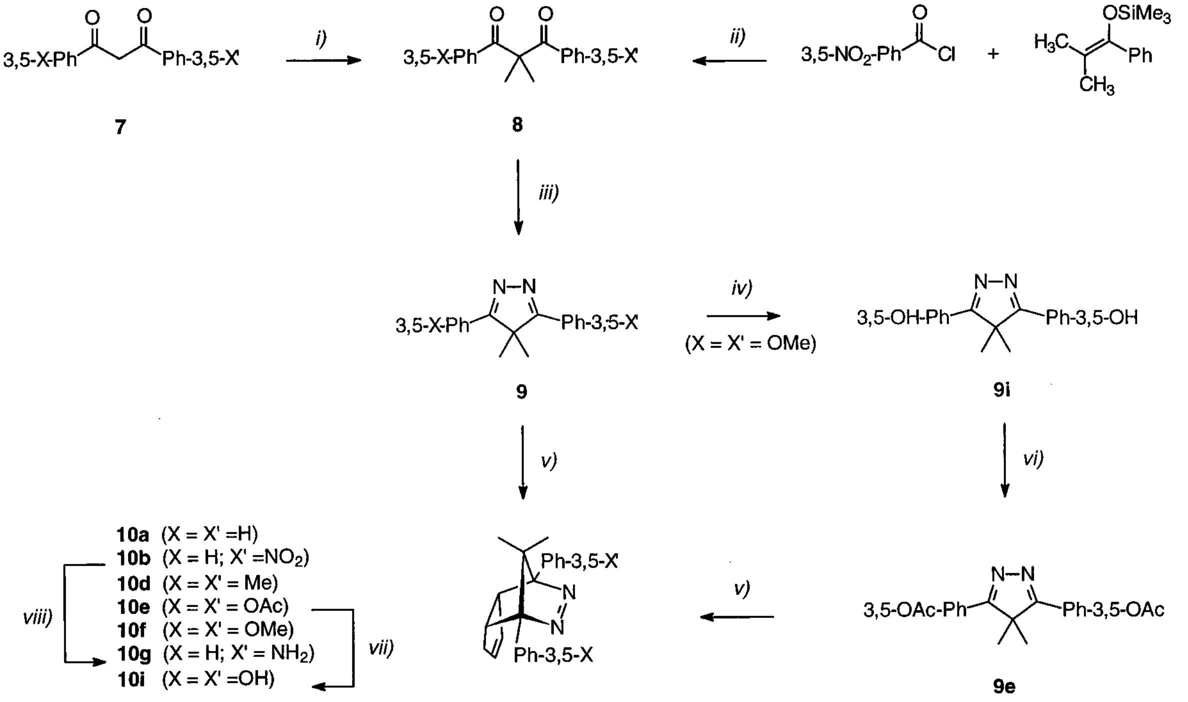
Scheme 1



i) K_2CO_3,CH_3I (excess), DMSO/$CHCl_3$, ca. 20 °C, 48 h; *ii)* $TiCl_4$ (5 equiv.), CH_2Cl_2, -78 °C → ca. 20 °C; *iii)* $N_2H_5{\cdot}H_2O$ (1.5 equiv.), $CHCl_3$, reflux, 15 h; *iv)* BBr_3 (5 equiv.), CH_2Cl_2, 0 °C → ca. 20 °C, 5 h; *v)* CF_3COOH (0.9 equiv.), Cyclopentadiene, CH_2Cl_2, 0 °C, 24 h; *vi)* $(AcO)_2O$ (2.2 equiv.), CH_2Cl_2, reflux, 5 h; *vii)* $N_2H_4{\cdot}H_2O$ (2.2 equiv.), CH_2Cl_2, reflux, 4h; *viii)* PtO_2, H_2, ethyl acetate, ca. 20 °C, 24 h.

Nevertheless, the direct comparison between the EPR α hyperfine coupling constants of the benzyl radicals **1** and **2** showed a rather poor additivity effect [$a_\alpha(\mathbf{2}) = 1.34 \pm 0.23\ a_\alpha(\mathbf{1})$, $r^2 = 0.893$, $n = 7$].[10] The same tendence has been noticed earlier in the novel μSR technique for muonated *meta*-disubstituted cyclohexadienyl radicals, which have been considered to be isoelectronic with the benzyl radicals.[11] Thus, we were interested to probe rigorously the additivity of the electronic influence of two *meta*-substituents on benzyl-type monoradicals, for which the *D* parameter of the corresponding triplet diradicals **6** should constitute a convenient and accurate measure. The results on the *D* parameter of the triplet diradicals **6** are given in the present report and demonstrate convincingly the additivity of electronic effects in *meta*-disubstituted benzyl-type radicals.

Results and Discussion

Synthesis. The synthesis of the azoalkanes **10** was conducted in analogy to previously reported procedures.[3b,d,12] This synthetic route was not feasible for the derivatives **10b** ($X = H$; $X' = NO_2$), **10g** ($X = H$; $X' = NH_2$), and **10i** ($X = X' = OH$). Therefore, the unsymmetric diketone **8b** was synthesized by the $TiCl_4$-catalyzed addition of 3,5-dinitrobenzoyl chloride to the trimethylsilyl enol ether of isobutyrophenone (Scheme 1).[13] The azoalkane **10g** was obtained by catalytic hydrogenation of the derivative **10b** on PtO_2 as catalyst. In turn, saponification of the derivative **10e** yielded the hydroxy-substituted azoalkane **10i**.

Table 1. Zero-Field-Splitting Parameter *D* and Δ*D* Values of the 3,3′,5,5′-Tetrasubstituted Triplet Diradicals 6 and Calculated α Spin Densities (ρ_α) for the 3,5-Disubstituted Cumyl Monoradicals 4

	X	X′	|*D*/*hc*| of **6**[a]	ρ_α of **4**[b]	Δ*D*[c]
a	H	H	0.0504	0.542	0.00
b	H	NO_2	0.0511		
c	NO_2	NO_2	0.0518[d]	0.546	−0.14
d	CH_3	CH_3	0.0524	0.549	−0.20
e	OAc	OAc	0.0527	0.551	−0.23
f	OCH_3	OCH_3	0.0538	0.558	−0.34
g	H	NH_2	0.0525		
h	NH_2	NH_2	0.0545[d,e]	0.563	−0.39
i	OH	OH	0.0547	0.563	−0.43

[a] Measured in a MTHF glass matrix at 77 K, values given in cm^{-1}, error ± 0.0001 cm^{-1}, for the triplet diradicals **6**, $|E/hc| < 0.001\ cm^{-1}$. [b] Calculated α spin densities for the cumyl monoradicals; *cf.* the text. [c] Calculated according to eq 2, values given in $10^2\ cm^{-1}$. [d] Calculated according to eq 3 from the unsymmetrically disubstituted diradicals; *cf.* the text. [e] The *D* value is 0.0506 cm^{-1} for the parent triplet diradical without an olefinic double bond.

EPR Spectroscopy. The triplet diradicals **6** were generated in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K by means of irradiation with the 364-nm line of an argon ion laser. The results of the low-temperature EPR measurements are summarized in Table 1. The smallest *D* value (0.0511 cm^{-1}) is found for the *unsymmetrically* disubstituted derivative **6b** ($X = H$; $X' = NO_2$) with the strong electron-accepting 3,5-nitro groups, whereas the largest *D* value (0.0547 cm^{-1}) is observed for the hitherto unknown triplet diradical **6i** ($X = X' = OH$) with four strongly electron-donating *meta*-hydroxy groups. In view of the recently shown[3b] additivity of electronic substituent effects on radical sites, the *D* parameters for the as yet unknown *symmetrically* tetrasubstituted derivatives **6c** ($X = X' = NO_2$, 0.0518 cm^{-1}) and **6h** ($X = X' = NH_2$, 0.0545 cm^{-1}) may be assessed.

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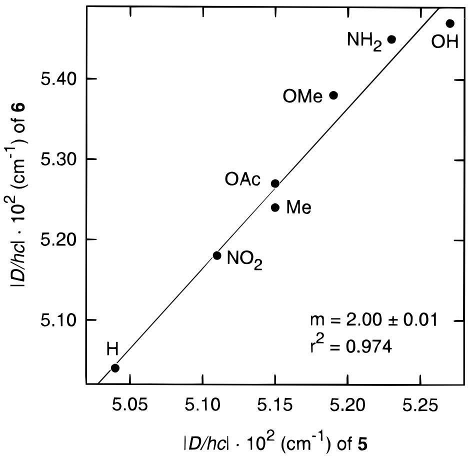


Figure 1. The experimental D values of the 3,3′,5,5′-tetrasubstitute (**6**) *versus* the 3,3′-disubstituted (**5**) triplet diradicals.

For this purpose eq 3 applies and the experimental D

$$D_{\mathrm{H,X}} = \sqrt{D_{\mathrm{X,X}} D_{\mathrm{H,H}}} \qquad (3)$$

values of the *unsymmetrical* derivatives **6b** (X = H; X′= NO_2) and **6g** (X = H; X′ = NH_2; *cf.* Table 1) were used as input data.[3d]

The Additivity of Electronic *Meta*-Substituent Effects. Table 1 reveals that all 3,3′,5,5′-tetrasubstituted triplet diradicals **6** possess large negative ΔD values, and consequently, the α spin density in the corresponding 3,5-disubstituted cumyl monoradicals **4** is increased (eq 1). Thus, strong electron-donating (ED) groups such as NH_2 or OH at both *meta*-positions destabilize the benzylic radical center efficiently, whereas this effect is only moderate for strong electron-accepting (EA) groups, *e.g.* NO_2. The composite electronic effects of two *meta*-substituents in each phenyl ring of the diradicals **6** is destinctly *larger* than previously observed for only one *meta*-substituent in the diradicals **5**[3c,d] and implicates that an electronic *additivity* effect operates also for two *meta*-substituents in the cumyl monoradicals **4**. The plot of the experimental D parameter of the 3,3′,5,5′-tetrasubstituted triplet diradicals **6** *versus* the D parameter of the corresponding 3,3′-disubstituted triplet diradicals **5** (Figure 1) confirms this in the form of the excellent linear dependence ($r^2 = 0.974$) and the slope of $m = 2.00 \pm 0.01$. Furthermore, semiempirical MO calculations (PM3-AUHF) corroborate this additivity by the linear plot of the calculated α spin densities for the monoradicals **3** and **4** against the experimental D parameters of the corresponding triplet diradicals **5** and **6** (Figure 2, $|D/hc| \times 100 = 16.4\rho_\alpha{}^2 + 0.3$, $n = 13$). Additionally, the linear correlation ($r^2 = 0.991$) of the calculated α spin densities of the 3,5-disubstituted cumyl radicals **4** *versus* the 3-substituted radicals **3**[3d] with a slope of $m = 2.00$ (figure not shown) substantiates once more the additivity of electronic effects in the cumyl monoradicals exerted by *meta*-substituents.

Simple Hückel theory predicts that *meta*-substituents in the benzyl-type radicals should exhibit no significant effect on the α spin density. Nevertheless, it is known that detectable spin density is found at the *meta*-positions in the ground state of such radicals, *i.e.* $a_{\mathrm{meta}} = 1.70$ G for the parent benzyl **1** and $a_{\mathrm{meta}} = 1.65$ G for the parent cumyl radical **3**.[8] Evidently, the radical site and the *meta*-substituents are connected through the π system of the benzene ring. Thus, in these cross-conjugated systems the electronic effects of the α spin center and the *meta*-substituent compete with one another for conjugation with the aromatic ring at the *ortho*- and *para*-positions such that the resulting effect is *spin localization* at the benzylic radical site. This interplay may be demonstrated by the semiempirically calculated spin densities in Figure 3, which reflect the localization of α spin density at the benzylic position with increasing substitution at the phenyl moiety. While the α spin density increases only moderately ($\Delta\rho_\alpha = 0.004$) for the strongly electron-accepting NO_2 group, these calculations reveal a substantial increase ($\Delta\rho_\alpha = 0.021$) for the strongly electron-donating OH substituent in the cumyl radicals **3** and **4**. This is in line with our recent report that the destabilizing effect of *meta*-substituents in the cumyl radicals **3** depends on the electron-donating propensity of such substituents[3d] and even holds true for the *meta*-isomers of hetaryl substituents.[14]

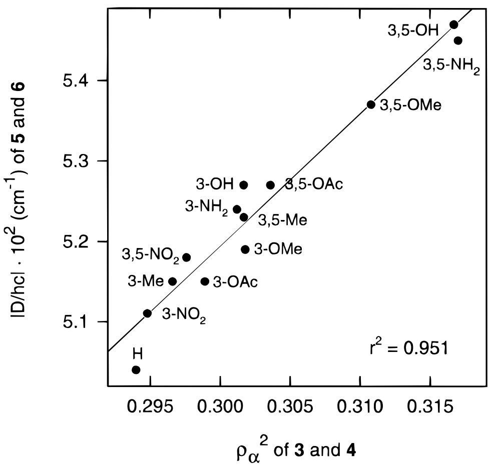
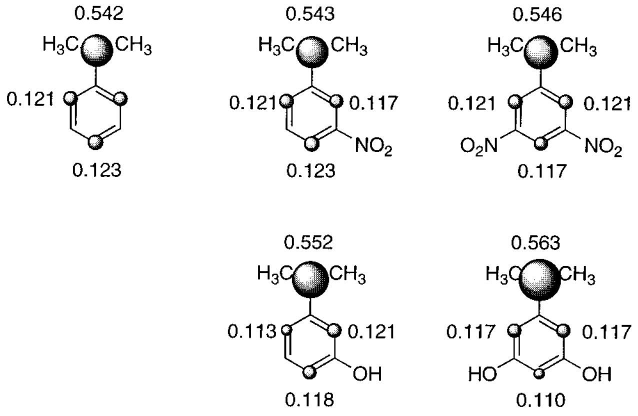


Figure 2. The experimental D values of the triplet diradicals **5** and **6** *versus* the calculated (PM3-AUHF/CI) α spin densities of the cumyl radicals **3** and **4** (*cf.* ref 3c).



3 **4**

Figure 3. Calculated (PM3-AUHF/*CI*) α spin densities for the parent cumyl radical (left), the 3-monosubstituted **3** (center), and the 3,5-disubstituted cumyl radicals **4** (right).

A previous EPR study of the *meta*-disubstituted benzyl radicals **2** by Jackson[10] reported a rather poor additivity ($r^2 = 0.893$, $m = 1.34 \pm 0.23$) for the α hyperfine coupling constants when compared to the *meta*-monosubstituted

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benzyl radicals **1**.[8] Moreover, UMINDO calculations showed no significant changes in the α spin density for the *meta*-disubstituted benzyl radicals **2**.[10] However, the employed *meta*-substitutents, namely CF_3, F, ^{t}Bu, Cl, Me and OMe, cover only a relatively small range of electronic effects in their destabilizing ability on benzyl-type radicals,[3d] which presumably is responsible for the considerable scatter in the experimental data. In contrast, the readily accessible *D* parameter of the triplet diradicals **6** constitutes an accurate measure of electronic effects on such radical sites (eq 1) and the featured substituents span the whole range from strongly electron-accepting (NO_2) to strongly electron-donating (NH_2) groups, an advantage of our ΔD substituent scale which is not offered by any of the other σ_{rad} scales.[4−8]

Conclusions

A set of 3,3′,5,5′-tetrasubstituted triplet diradicals **6**, which features strong electron acceptors (NO_2) as well as strong electron donors (OH), has been used for a detailed study of the *meta*-substituent additivity in the corresponding 3,5-disubstituted cumyl radicals **4**. The slope of $m = 2.00$ in the excellent correlation between the *D* parameters of the triplet diradicals **6** and the 3,3′-disubstituted triplet diradicals **5** shows unequivocally the *additivity* of electronic *meta*-substituent effects, which is further substantiated by semiempirical MO calculations for the corresponding 3-substituted cumyl radicals **4**. Thus, the EPR-spectroscopic *D* parameter of localized cyclopentane-1,3-diyl triplet diradicals provides for the first time a convenient tool to probe for hitherto unknown synergistic or antagonistic substituent effects in multiply substituted benzyl-type monoradicals.

Experimental Section

EPR Spectroscopy. A sample (*ca.* 5×10^{-4} mmol) of the corresponding azoalkane was dissolved in 0.3 mL of MTHF, placed into an EPR sample tube (∅ *ca.* 2 mm) and thoroughly degassed by purging with argon gas. The samples were sealed and the 77-K matrix was prepared by freezing the samples in liquid nitrogen. The triplet diradicals **6** were generated by irradiation with the 364-nm line of an INNOVA-100 CW argon-ion laser (widened beam, 1.5 W, 2 min) at 77 K, and their EPR spectra were recorded on a Bruker ESP-300 spectrometer (9.43 GHz, spectra accumulation with the Bruker 1620 Data-System, $n \geq 5$). The *D* values were determined by a manual analysis of the Z signals.

Computations. Full geometry optimization of the cumyl radicals **3** and **4** was carried out on the highest molecular symmetry, *i.e.* C_{2v} symmetry, for all disubstituted radicals **4** by using the semiempirical PM3 method[15] and the annihilated UHF wavefunction provided in the *VAMP 5.0* program package[16] and run on a IRIS INDIGO R4000 Silicon Graphics workstation. The spin densities were determined by a single point CI (5 × 5) calculation to afford excellent $\langle S^2 \rangle$ values of 0.77−0.79.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Synthetic details and characteristic spectral data of the 1,3-propanediones **7**, 2,2-dimethyl-1,3-propanediones **8**, 4,4-dimethyl-4*H*-pyrazoles **9**, and the azoalkanes **10** (7 pages). This material is contained in libraries on michrofiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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