The EPR-Spectral *D* Parameter of Photochemically Generated Cyclopentane-1,3-diyl Triplet Diradicals as a Quantitative Measure of Spin Delocalization in Vinyl-, Phenyl-, and Carbonyl-Substituted Radicals

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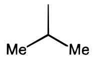
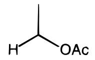
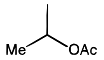
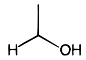
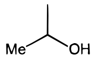
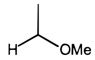
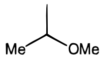
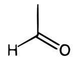
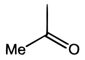
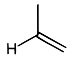
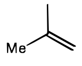
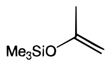
The zero-field splitting parameter *D* of the localized cyclopentane-1,3-diyl triplet diradicals **T**, generated in a 2-methyltetrahydrofuran (MTHF) glass matrix at 77 K through photochemical deazetation of the corresponding azoalkanes **1**−**13**, has been determined by EPR spectroscopy. It is demonstrated that the *D* parameter reliably reflects the changes caused by the alkyl (simple and oxyfunctionalized), vinyl, and carbonyl substituents of the spin densities at the radical site. Thus, spin delocalization of the substituents and stabilization of the radical center follow the order vinyl > phenyl > carbonyl ≫ alkyl. This trend is confirmed by the excellent linear correlations with the reported α-hyperfine coupling constants (α-hfc) of the corresponding monoradicals and computed semiempirical (PM3 method) spin densities of the radical fragments **M**.

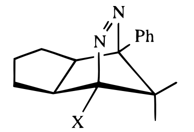
Introduction

The photochemical deazetation of diazabicyclo[2.2.1]-heptene (DBH) derivatives conveniently generates cyclopentane-1,3-diyl triplet diradicals, which are persistent in low-temperature matrixes.[1] These intermediates may be detected by EPR spectroscopy and are characterized by the zero-field-splitting (zfs) parameters *D* and *E*.[1] For such localized triplet 1,3-diradicals, the *D* parameter (the dipolar interaction between the radical termini) depends on the interspin distance d_{ab} and the spin densities ρ_a and ρ_b at the respective radical sites a and b (eq 1, where $\rho_a = \rho_X$ and $\rho_b = \rho_{Ph}$). The spin density[2a,b] as well as the distance dependence[2c] have been confirmed experimentally and theoretically. At a constant d_{ab} distance, the *D* parameter is a sensitive probe of electronic substituent effects through the α spin density ρ_X and provides a measure of radical stabilization in terms of the efficiency of spin delocalization.

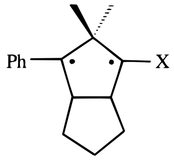
$$D = \frac{3\mu_0 g^2 \mu_B^2}{16\pi}\left(\frac{\rho_a \rho_b}{d_{ab}^3}\right) \qquad (1)$$

The interest of the present study was to examine the electronic influence of alkyl, vinyl, and carbonyl substituents on the *D* parameter in triplet 1,3-diradicals. Specifically, the spin-delocalizing propensity of these substituents was to be assessed and compared with that of the phenyl group. We now report the EPR-spectral data for the unsymmetrical diradicals **T**, generated photolytically from the azoalkanes **1**−**13**. These results demonstrate unequivocally that the *D* parameter reliably measures the spin-delocalizing properties of vinyl and carbonyl substituents, as confirmed by experimental

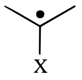
T, M	X
1	$-CH_3$
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	



1 - 13



T



M

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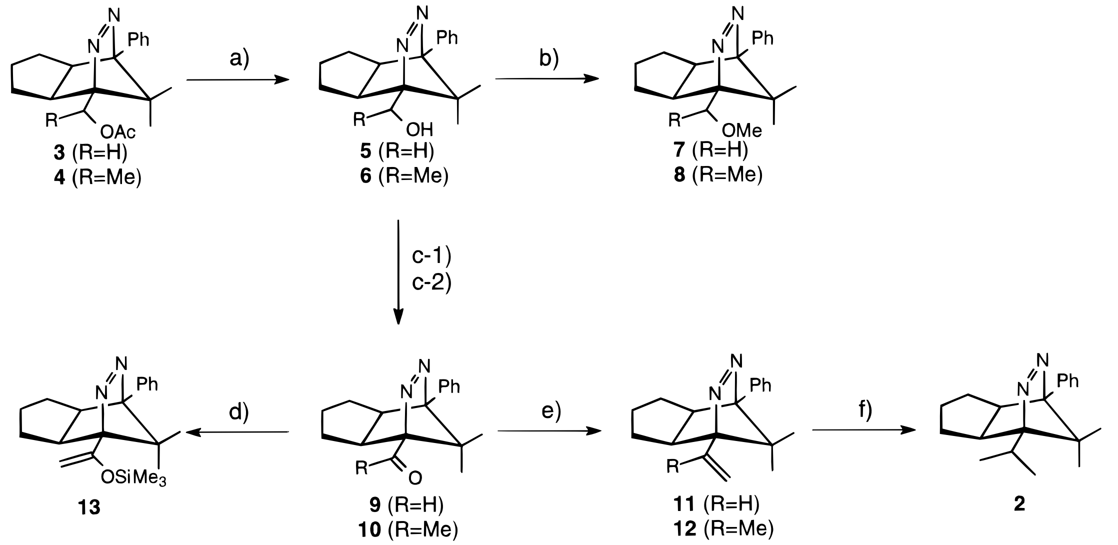
10.1021/jo9817422 CCC: $18.00

Scheme 1. Synthesis of the Azoalkanes 2−13[a]



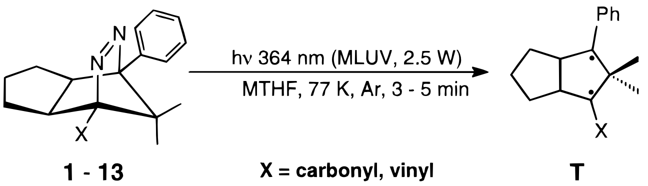
[a] Key: (a) K_2CO_3, MeOH, 20 °C, 18 h; (b) KOH, excess MeI, DMSO, 20 °C, 12 h; (c-1) DCC, H_3PO_4, DMSO, 20 °C, 18 h; (c-2) PCC, CH_2Cl_2, 20 °C, 5 h; (d) LDA, Me_3SiCl, THF, −78 to 20 °C, 3 h; (e) $Ph_3P{=}CH_2$, toluene, 20 °C, 24 h; (f) H_2, Pd/C, EtOAc, 20 °C, 48 h.

(hyperfine coupling constants)[3] and theoretical (ab initio computations)[4] literature data for the corresponding monoradicals **M**.

Results

Synthesis. The known azoalkane **1** was prepared according to the literature procedure,[5] the unknown ones **3** and **4** analogously through acid-catalyzed cycloaddition of the corresponding 4,4-dimethyl-5-phenyl-4*H*-pyrazoles with cyclopentadiene (for details cf. the Supporting Information).[6] Saponification of azoalkanes **3** and **4** gave the hydroxy-substituted derivatives **5** and **6** (Scheme 1); methylation of the latter yielded the methoxy-substituted azoalkanes **7** and **8**. The azoalkanes **9** and **10** were made by oxidation of **5** (Pfitzner−Moffat[7]) and **6** (pyridinium chlorochromate[8]). Wittig reaction of the azoalkanes **9** and **10** with an excess of methylenetriphenylphosphorane led to the alkenyl-substituted derivatives **11** and **12**.[9] Catalytic hydrogenation of azoalkane **12** gave the propyl-substituted azoalkane **2**. Deprotonation of azoalkane **10** with LDA and reaction with trimethylsilyl chloride afforded the silyl enol ether **13**.[10]

Scheme 2. Photochemical Generation of the Cyclopentane-1,3-diyl Triplet Diradicals T



EPR Spectroscopy. The triplet diradicals **T1−13** were obtained by direct irradiation of the corresponding azoalkanes in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K (Scheme 2) with an argon-ion laser (364 nm); they persisted for several hours at 77 K. In all cases, the half-field signal ($\Delta m_s = \pm 2$), characteristic for triplet states, was located at 1650−1680 G, whereas the relevant diradical *z* signals in the $\Delta m_s = \pm 1$ region were located at $B_{min} = 2841 \pm 60$ G and $B_{max} = 3924 \pm 60$ G at a microwave frequency of 9.43 GHz. The *E* parameter of the triplet diradicals was very small, and thus, only an upper limit (≤ 0.001 cm^{-1}) may be given.

The results in Table 1 reveal for the triplet diradicals a significant dependence of the zero-field splitting parameter *D* on the electronic nature of the substituent.

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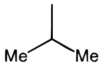
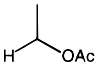
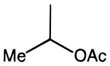
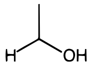
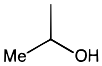
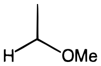
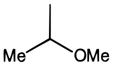
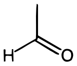
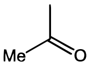
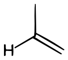
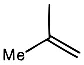
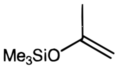
Table 1. Experimental[a] Zero-Field EPR Data |*D/hc*| of the Matrix-Isolated Triplet Diradicals T1−13

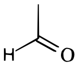
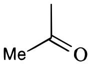
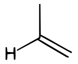
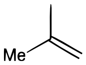
	X	|*D/hc*| [b)]
T1	$-CH_3$	0.0671
T2		0.0672
T3		0.0660
T4		0.0672
T5		0.0668
T6		0.0668
T7		0.0663
T8		0.0669
T9		0.0535
T10		0.0555
	- Ph [c)]	0.0506
T11		0.0473
T12		0.0477
T13		0.0483

[a] Recorded at 77 K in a 2-methyltetrahydrofuran (MTHF) matrix. [b] Values given in cm^{-1}, accuracy ± 0.0001 cm^{-1}. [c] As reference system.

The largest *D* values (least delocalization) are observed for the alkyl-substituted diradicals **T1,2** (ca. 0.067 cm^{-1}), whereas the olefinic derivatives **T11−13** (0.047−0.048 cm^{-1}) possess the smallest ones (most delocalization). The oxyfunctionalized alkyl substituents in the diradicals **T3−8** (Table 1) show only nominal (0.0666 ± 0.006 cm^{-1}), if at all significant, changes on the *D* value. However, pronounced effects are witnessed for the carbonyl derivatives **T9**,**10** (0.0545 ± 0.010 cm^{-1}) and the vinyl derivatives **T11−13** (0.0478 ± 0.050 cm^{-1}). Clearly, the exchange of the CH_2 group for an O atom leads to higher *D* values and implies greater spin delocalization for the vinyl versus the carbonyl substituent.

Computations. The geometry optimization of the model monoradicals **M** was carried out by using the semiempirical PM3 method with annihilated UHF wave functions provided in the VAMP 5.0 program package[11] and run on a IRIS INDIGO R4000 Silicon Graphics workstation, which gave for all the **M** derivatives excellent $\langle S^2 \rangle$ values of 0.750, as expected for pure doublet ground states. The spin densities were determined by a single-point CI calculation to afford good $\langle S^2 \rangle$ values between 0.752 and 0.761.[12] The ρ_α values are listed in Table 2.

Table 2. Comparison of the Experimental α Spin Densities Calculated from the *D* Parameter and the α-hfc Values with the Theoretical Ones Computed by Semiempirical and ab Initio Methods

	spin densities			
	experimental		theoretical	
X	ρ_X(D) [a)]	ρ_X(hfc) [b)]	ρ_X(semi) [c)]	ρ_X(*ab*) [d)]
	0.623	0.681	0.712	0.709 (ref 4a)
	0.646	0.690	0.694	n. a.
	0.551	0.507	0.582	n. a.
	0.555	0.508	0.583	0.537 (ref 4b)
Ph	0.589	0.585	0.589	0.640 (ref 4c)

[a] ρ_X is the spin density at the radical site that bears the X substituent and ρ_{Ph} that at the phenyl-substituted center; calculated from the *D* values (Table 1) according to eq 1, with ρ_{Ph} = 0.589 and d_{ab} = 2.50 Å. [b] Calculated from the α-hfc data[3] according to eq 2. [c] Computed by the semiempirical AUHF/PM3 method. [d] Computed by ab initio method; n. a. stands for not available.

Discussion

These electronic effects of the substituents shall now be interpreted in terms of their spin-delocalizing propensity by analyzing the pertinent electronic structures assessed from computational and spectral data. Since inductive effects in the oxyfunctionalized derivatives **T3−8** play no significant role (*D* values are essentially constant at 0.067 cm^{-1}), we shall focus on the π delocalization in the carbonyl (**T9,10**) and vinyl (**T11,12**) systems and compare their efficiency with the phenyl substituent.

We assume that all diradicals **T1−13** possess the same planar geometry, as borne out by MO calculations (PM3),[13] which yield a direct energy minimum for the planar 1,3-cyclopentanediyl ring with coplanar substituents. The planarity of the 1,3-cyclopentanediyl ring is in line with earlier ab initio calculations for the 1,3-cyclobutanediyl[14] and the parent 1,3-cyclopentanediyl[15] diradicals. According to semiempirical computations (AM1 method), rotation of the substituents in the diradical requires an appreciable activation barrier (7 kcal/mol).[16a] Therefore, the observed changes in the *D* values are proposed to represent electronic effects by the substituents on the spin delocalization in the monoradical

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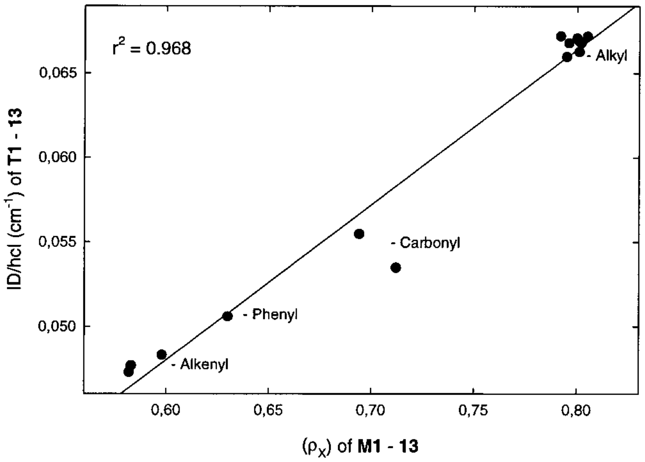

Figure 1. Experimental *D* values of the triplet diradicals **T** versus the theoretical (PM3-AUHF) α spin densities (ρ_X) of the corresponding monoradical fragments **M**.

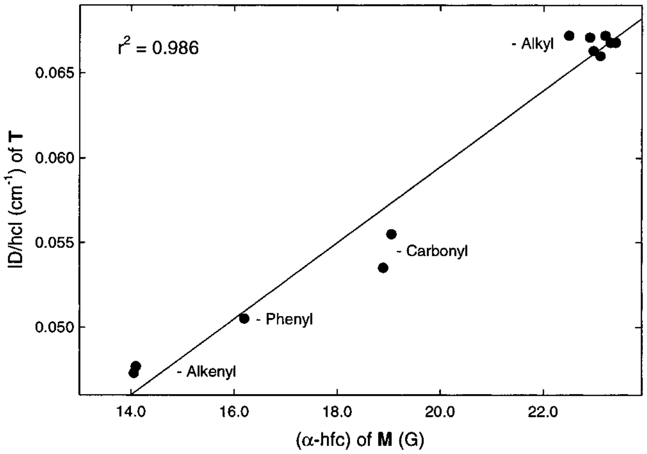

Figure 2. Experimental *D* parameter of the triplet diradicals **T** versus reported α-hyperfine coupling constants (α-hfc) of the corresponding monoradicals **M**.

fragment **M** rather than variations in the conformational features of the triplet diradicals **T**.[17]

The radical centers in the localized triplet 1,3-diradicals act independently of each other, except for the low-energy dipolar spin–spin interactions, as confirmed through the additivity of substituent effects in 1,3-diaryl-substituted derivatives.[16] Since in all the present unsymmetrical derivatives **T1**–**13** one radical site is kept constant (phenyl substitution), the experimentally assessed changes in the *D* parameter must derive from the substituent X at the other radical center. According to eq 1, the *D* value depends on the spin densities (ρ_X, ρ_{Ph}) of the radical sites and the interspin distance (d_{ab}).[16] This simple relationship offers the opportunity to link the experimental *D* values of the triplet diradicals **T** with the theoretically accessible spin densities of the monoradicals **M** and evaluate thereby quantitatively the observed electronic substituent effects.

Indeed, as displayed in Figure 1, the experimental *D* values of the triplet diradicals **T** correlate impressively well ($r^2 = 0.968$, $n = 14$) with the calculated α spin densities of the monoradical fragments **M**. The experimental validity of this correlation is substantiated by the fact that an excellent ($r^2 = 0.986$, $n = 12$) linear correspondence is obtained when the *D* parameter of the triplet diradicals **T** is plotted against the reported α-hyperfine coupling constants (α-hfc)[3] of the corresponding monoradicals **M** (Figure 2). This correspondence rests on the fact that according to the McConnell relation (eq 2) the α-hfc values constitute an established experimental measure of the spin densities, which has been widely used in the past for monoradicals.[3]

$$a_\alpha = Q_\alpha \rho_\pi \quad \text{with } Q_\alpha = 23.04\text{ G} \tag{2}$$

Consequently, the *D* parameter provides a reliable quantitative measure of spin delocalization by substituents in the triplet diradicals **T**, and through the semiempirical spin densities (ρ_X) at the radical sites, valuable information on the electronic structure of the monoradicals **M** become accessible. This may be nicely illustrated for the vinyl- and carbonyl-substituted triplet diradicals **T9**–**12** (Table 1). Comparison of the *D* values with that of the phenyl derivative clearly demonstrates that spin delocalization by the X substituents at the radical site follows the order vinyl > phenyl > carbonyl. This trend matches well the one established in the literature for the monoradicals by α-hfc data[3] and theoretically by ab initio calculations (Table 2).[4] For ease of comparison with the theoretical spin densities ρ_X(semi) and ρ_X(*ab*) in Table 2, the experimental spin densities ρ_X(D) and ρ_X(hfc) have been calculated from the *D* data according to eq 1 (with constant d_{AB} and ρ_{Ph}) and α-hfc data according to eq 2. Clearly, qualitatively all four ρ_x parameters reproduce adequately the vinyl > phenyl > carbonyl order in delocalizing spin at a radical center, but quantitatively the best correspondence is displayed between the experimental ρ_X(D) and theoretical ρ_X(semi) values, as was already shown in the good linear correlation of Figure 1. The discrepancies in the correlation with the experimental ρ_X(hfc) values may in part derive from the fact that these data have been measured at different reaction conditions.

The efficacy of spin delocalization for the substituents vinyl > phenyl > carbonyl, confirmed here by the *D* parameter of the triplet diradicals T, implies that these radicals are accordingly stabilized. That this is the case is displayed by the theoretical radical stabilization energies (RSE), which follow the order allyl (14.4 kcal/mol)[18] > benzyl (12.0 kcal/mol)[19] > carboxaldehyde (ca. 5.5 kcal/mol).[18,20] Thus, a carbonyl group is substantially less (by ca. 9 kcal/mol) effective in delocalizing spin than the vinyl substituent. Radicals are electron-deficient species, and hence, the electronegative oxygen atom resists delocalization to form the carboxaldehyde radical.[20] Nevertheless, the carbonyl-substituted radicals **M9,10** are considerably more delocalized (Table 1) and, thus, stabilized than the alkyl-substituted radicals **M1**–**8** (with and without oxygen functionalizations).

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In summary, we reiterate that the *D* parameter, which is accurately determinable by EPR spectroscopy for the readily prepared cyclopentane-1,3-diyl triplet diradicals examined herein, serves as reliable and convenient spectroscopic measure of electronic substituent effects in monoradicals. The good correspondence with known α-hfc[3] and theoretical data[4] is gratifiying and encourages to apply the *D* parameter as mechanistic tool for the aquisition of electronic and structural information about unpaired-spin species.

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Supporting Information Available: Synthetic details and characteristic spectral data of 1,3-pentanediones, 2,2-dimethylpentanediones, 4,4-dimethyl-4*H*-pyrazoles and the azoalkanes **2**−**13** are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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