

The *D* Parameter of Vinyl-Substituted 1,3-Cyclopentanediyyl Triplet Diradicals as a Sensitive Tool To Determine Electronic Substituent Effects in Allylic Radicals

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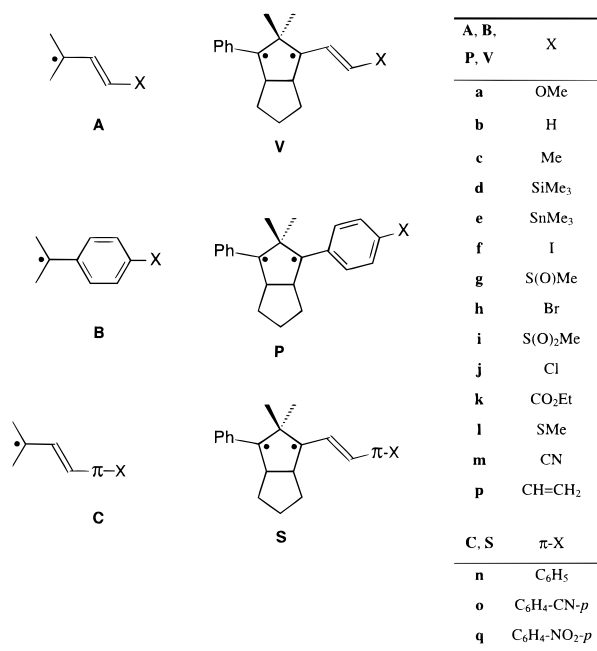
The zero-field *D* parameter of the localized vinyl-substituted 1,3-cyclopentanediyyl triplet diradicals **V** was determined at 77 K in a 2-methyltetrahydrofuran (2-MTHF) glass matrix. Good linear correlations were obtained with the reported α -hyperfine coupling constants ($r^2 = 0.991$, $n = 7$) and with the semiempirically calculated (PM3) spin densities ($r^2 = 0.989$, $n = 16$) of the corresponding allylic monoradicals **A**. The observed substituent effects are generally larger and, thus, more accurately measured compared to the previously examined aryl-substituted 1,3-cyclopentanediyyl triplet diradicals **P**. The vinyl-substituted triplet diradicals reflect accurately the delocalizing propensity of substituents, either through hyperconjugative, mesomeric, or inductive effects. For the methyl group, the small but significant stabilization of adjacent radical sites has been clearly demonstrated. In the case of the halogen set, the small but definitive heavy-atom effect has been determined for the bromo (0.0010 cm⁻¹) and the iodo (0.0024 cm⁻¹) substituents. The organometallic substituents SiMe₃ and SnMe₃ are shown to be weak spin acceptors, while spin delocalization for the sulfur series follows the increasing order MeS \gg MeSO₂ > MeSO.

Introduction

Triplet diradicals are conveniently generated through photochemical deazetation of the corresponding azoalkanes.^{1,2} The resulting 1,3-cyclopentanediyyl triplet diradicals³ are persistent in matrices at 77 K, detectable by EPR spectroscopy, and characterized by the zero-field splitting (zfs) parameters *D* and *E*, of which *D* provides information on electronic effects in radicals.^{2,4} The *D* parameter is given by eq 1,⁵

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

which we have confirmed experimentally,^{6,7} where ρ_a and ρ_b are spin densities at the radical sites a and b and d_{ab} is the interspin distance. The aim of the present study was to elucidate electronic substituent effects in allylic radicals since relatively little is to date known.⁸ We have recently developed the necessary synthetic methodology⁹ to prepare the vinyl-substituted triplet diradicals **V** to assess electronic substituent effects in the corresponding allylic radical fragments **A**. For this purpose, first the



quality and magnitude for the styryl-substituted 1,3-cyclopentanediyyl triplet diradicals **S** were to be determined and compared with that of the already reported⁵ corresponding phenyl cases **P**. This comparison would provide a direct measure of the efficacy of spin delocalization in the benzyl-type monoradical fragments **B** and the corresponding phenyl derivatives **C**. The substituent

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(1) Borden, W. T. *Diradicals*; Plenum Press: New York, 1978.

(2) Dougherty, D. A. In *Kinetics and Spectroscopy of Carbenes and Diradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; pp 117–142.

(3) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688–4694.

(4) a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice Hall: Englewood Cliffs, 1969. (b) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; Wiley: New York, 1994.

(5) Adam, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Adv. Photochem.* **1998**, *24*, 205–254.

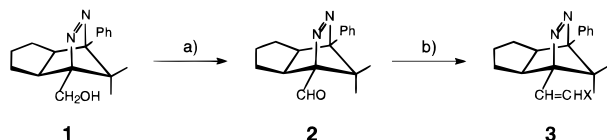
(6) Adam, W.; van Barneveld, C.; Emmert, O. *J. Chem. Soc., Perkin Trans. 2* **2000**, 637–641.

(7) Adam, W.; Emmert, O.; Harrer, H. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 687–694.

(8) (a) Butcher, E.; Rhodes, C. J.; Standing, M.; Davidson, R. S.; Bowser, R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1469–1474. (b) MacInnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1073–1076. (c) Griller, D.; Ingold, K. U.; Walton, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 758–759. (d) Sustmann, R.; Trill, H.; Vahrenholt, F.; Brandes, D. *Chem. Ber.* **1977**, *110*, 255–263.

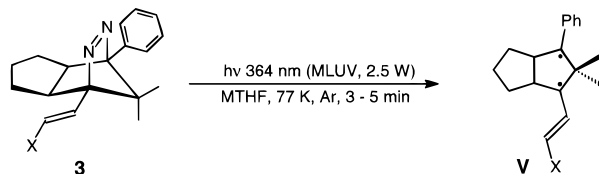
(9) Adam, W.; Emmert, O.; Heidenfelder, T. *J. Org. Chem.* **1999**, *64*, 3417–3421.

Scheme 1. Synthesis of the Vinyl-Substituted Azoalkanes 3a–q



a) 1. $C_2O_2Cl_2$, DMSO, CH_2Cl_2 , $-60\text{ }^\circ C$, 2 h; 2. NEt_3 , $-60\text{--}20\text{ }^\circ C$, 2 h;
b) $Ph_3P=CHX$, toluene or THF, $20\text{--}40\text{ }^\circ C$, 24–72 h.

Scheme 2. Photochemical Generation of the 1,3-Cyclopentanediyil Triplet Diradicals V



X = OMe, H, Me, SiMe₃, SnMe₃, I, SMe, Br, SO₂Me, Cl, CO₂Et, SMe, CN, C₆H₅, C₆H₄-CN-*p*, CH=CH₂, C₆H₄-NO₂-*p*

X is to be located directly on the vinyl group as in the V-type triplet diradicals, to answer the following questions on electronic substituent effects: (a) Do the allylic radical fragments A amplify the interaction between the radical site and the substituent X? (b) May herewith weak interactions (alkyl groups) be reliably assessed? (c) Is the methoxy substituent localizing the spin density, as we have implied in previous work in the phenyl-substituted series? (d) Are heavy-atom effects operating in the halogen set Cl, Br, and I? (e) How effective are sulfur functionalities (sulfanyl, sulfoxyl, and sulfonyl) in their spin-delocalizing propensity? (f) What is the influence of organometallic substituents?

Results

Synthesis. The azoalkanes were synthesized according to literature procedures.¹⁰ Oxidation of the hydroxymethyl-substituted azoalkane **1** was optimized by using the Swern¹¹ rather than the Pfitzner–Moffat oxidation¹² (Scheme 1), to afford the aldehyde **2** almost quantitatively. Wittig olefination of the latter with an excess of the appropriate phosphorane gave the azoalkanes **3** as a mixture of *E* and *Z* diastereomers; addition of lithium salts favored the formation of the *E* isomers.¹³

EPR Spectroscopy. The diradicals **V** were generated in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K by irradiation of the azoalkanes **3** with the 364-nm line of an argon-ion laser (Scheme 2). All diradicals persisted at this temperature as evidenced by constant EPR signals even beyond 12 h. The results of the EPR measurements are summarized in Table 1, with the *D* values arranged in descending order. Hence, the smallest *D* value is found for the *p*-nitrophenyl-substituted diradical **Vq** (0.0326 cm⁻¹), and the highest one is found for the methoxy-substituted vinyl derivative **Va** (0.0480 cm⁻¹). A pronounced dependence of the experimental *D* value on the substituent is evident, which is generally larger than

Table 1. Experimental Zero-Field *D* Values of the Matrix-Isolated Triplet Diradicals Va–q and the Theoretical Spin Densities of the Corresponding Monoradicals A

V, A	X	$ D/hc $ (cm ⁻¹) ^a V	spin densities (ρ) ^b A
a	OMe	0.0480	0.577
b	H	0.0473	0.573
c	Me	0.0456	0.551
d	SiMe ₃	0.0451	0.548
e	SnMe ₃	0.0450	0.540 ^c
f	I	0.0450	0.531
g	SOMe	0.0447	0.530
h	Br	0.0446	0.523
i	SO ₂ Me	0.0442	0.520
j	Cl	0.0437	0.514
k	CO ₂ Et	0.0413	0.486
l	SMe	0.0407	0.479
m	CN	0.0400	0.474
n	C ₆ H ₅	0.0357	0.430
o	C ₆ H ₄ -CN- <i>p</i>	0.0338	0.410
p	CH=CH ₂	0.0333	0.400
q	C ₆ H ₄ -NO ₂ - <i>p</i>	0.0326	0.390

^a Experimental *D* values were obtained from the EPR spectra recorded in 2-MTHF matrix, accuracy $\pm 0.0001\text{ cm}^{-1}$. ^b Spin densities were calculated for the monoradical fragments A by the semiempirical PM3 AUHF method, implemented in the VAMP 6.1 program package, ref 14. ^c Value estimated from Figure 2.

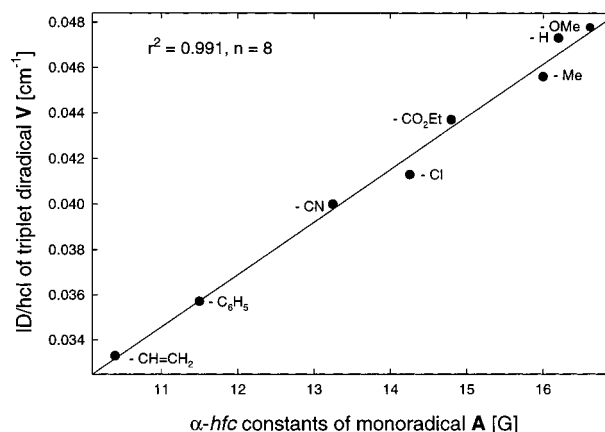


Figure 1. Experimental *D* values of the triplet diradicals **V** versus the reported α -hyperfine splitting constants (α -hfc) of the monoradical fragments **A**.

those previously observed for *meta* and *para* substituents on the aryl derivatives **P**.⁵

Discussion

We assume that all of these triplet diradicals have a planar geometry, as demonstrated by MO calculations (PM3)¹⁴ for the 1,3-cyclopentanediyil ring. In Figure 1, the *D* parameter of the triplet diradicals **V** is plotted against the reported α -hyperfine coupling constants (α -hfc)⁸ of the corresponding allylic monoradicals **A**. The excellent linear correlation ($r^2 = 0.991$, $n = 7$) between these two EPR-spectral parameters (*D* and α -hfc) demonstrates conclusively that the localized triplet diradicals **V** with substituents at the vinyl group reflect reliably the electronic substituent effects in allylic monoradicals. The α -hfc constant is a direct measure of the spin density in radicals,¹⁵ and in view of the good linear correlation in Figure 1, the *D* parameter of the triplet diradicals **V** reflects the changes in the spin density for the radical fragments **A** in terms of the efficacy of the electronic substituent to delocalize the unpaired electron.

(10) (a) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis* **1995**, 1163–1170. (b) Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 477–483.

(11) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651–1660.

(12) Pfitzner, K. E.; Moffat, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 5661–5670.

(13) Wittig, G.; Schlosser, M. *Chem. Ber.* **1961**, *94*, 1373–1383.

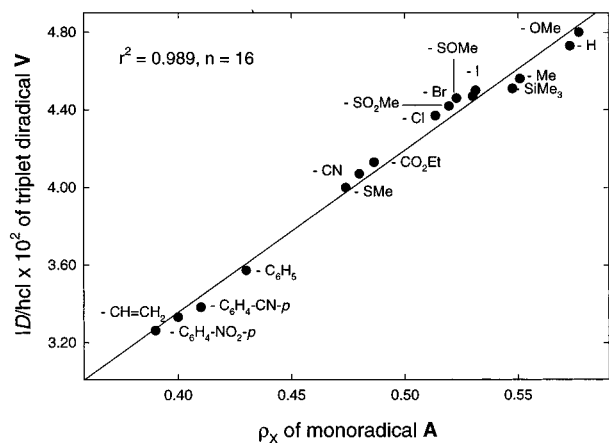


Figure 2. Experimental D values of the triplet diradicals **V** versus the theoretical (PM3, AUHF) α spin densities (ρ_X) of the corresponding monoradical fragments **A**.

Spin densities are theoretical quantities, which are readily assessed by semiempirical (PM3) calculations. For the triplet diradicals **V**, the excellent linear correlation ($r^2 = 0.989$, $n = 16$) of their experimental D values with the computed spin densities (ρ) at the radical sites of the corresponding monoradical fragments **A** (Figure 2) corroborates the functional dependence in eq 1. This good correspondence between the experimental and theoretical results establishes that the localized vinyl-substituted 1,3-cyclopentadienyl triplet diradicals **V** serve as a useful model system to evaluate electronic substituent effects in allylic monoradicals **A** analogous to the correspondence between the aryl-substituted triplet diradicals **P** and the respective cumyl monoradicals **B**.¹⁶

What about the efficacy of spin delocalization onto the styryl group in the **S** triplet diradicals versus the same set of substituents on the phenyl group in the **P** ones? For this purpose, the triplet diradicals **Sn** ($X = H$), **So** ($X = p\text{-CN}$), and **Sq** ($X = p\text{-NO}_2$) have been prepared and compared with the known **Pn** ($X = H$), **Po** ($X = p\text{-CN}$), and **Pq** ($X = p\text{-NO}_2$) set.

An excellent linear correlation ($r^2 = 0.9998$) is obtained between the D values of the **S** and the **P** sets, but more significant, the slope is unity! The absolute D values for these three triplet diradicals **Sn**, **So**, and **Sq** compared to the corresponding **P** ones are, however, consistently lower, i.e., $D_S - D_P = 0.0149 \text{ cm}^{-1}$ for the styryl (D_S) versus the phenyl (D_P) cases (cf. Table 1). This is due to the fact that the substituent in the **S** triplet diradicals acts on the spin density at the *para* position of a phenylallyl radical **C**, whereas for **P** the substituent is located at the *para* position of a benzyl radical fragment **B**. Even simple Hückel theory predicts that the spin density at the *para* position of the aryl group in the **S** diradical must be approximately half of that in **P**.¹⁷

From the above analysis it is clear that, for maximal changes of the D parameter, the substituent should be directly attached to the radical site, because spin density is then not "diluted" through the conjugation inherent with the π -type linker group, i.e., the styryl functionality

in the **S** species. The necessary preparative task turned out to be too difficult in the Hünig route,¹⁰ and the methodology exposed in Scheme 1 was employed. The substituent **X** is now π -connected to the radical site in the triplet diradicals **V**. The necessary azoalkanes **3** were prepared through Wittig–Horner olefination.

What would be the expected magnitude of the changes on the D parameter in such allylic versus benzylic fragments in the respective **V**- versus **P**-type triplet diradicals? Even simple Hückel theory provides an adequate answer for the parent allyl versus benzyl radicals. In the allylic radical the unpaired electron is distributed equally between the terminal positions and each carries one-half of the spin, while for the benzyl radical four-sevenths of the spin is located at the benzylic site and only one-seventh at the *para* position. Consequently, the electronic effects should be substantially amplified in the **V** species, and a considerably more sensitive probe for spin delocalization has therewith become available to enable sensing still smaller electronic effects.

In line with the previous experimental results obtained for the *p*-methoxyphenyl-substituted triplet diradical **Pa** ($D_{\text{OMe}} = 0.0510 \text{ cm}^{-1}$) versus the parent phenyl case **Pb** ($D_{\text{H}} = 0.0506 \text{ cm}^{-1}$)⁵ and for the methoxy-substituted derivative **Va** ($D_{\text{OMe}} = 0.0480 \text{ cm}^{-1}$) versus the unsubstituted parent system **Vb** ($D_{\text{H}} = 0.0473 \text{ cm}^{-1}$), an increased D value has been registered. There is, however, a significantly larger change for the **V** set ($D_{\text{OMe}} - D_{\text{H}} = 0.0007 \text{ cm}^{-1}$) than for the **P** set ($D_{\text{OMe}} - D_{\text{H}} = 0.0004 \text{ cm}^{-1}$). Since the D values are accurately measurable to within 0.0001 cm^{-1} , they constitute the most sensitive tool available for assessing electronic substituent effects in paramagnetic species.

A case on hand is the methyl substituent, notoriously a weak spin acceptor. The previous experimental results⁵ for the methyl-substituted triplet diradical **P** show only a slight spin delocalization by the methyl group ($D_{\text{Me}} = 0.0504 \text{ cm}^{-1}$ versus $D_{\text{H}} = 0.0506 \text{ cm}^{-1}$); in fact, the effect is lost in the experimental uncertainty. Nevertheless, a substantial influence is found for the methyl-substituted triplet diradical **Vc** versus the parent **Vb** ($D_{\text{Me}} = 0.0456 \text{ cm}^{-1}$ versus $D_{\text{H}} = 0.0473 \text{ cm}^{-1}$, i.e., $|D_{\text{Me}} - D_{\text{H}}| = 0.0017 \text{ cm}^{-1}$).

Similar small delocalizing effects are sensed for the organometallic substituents SiMe_3 in the triplet diradical **Vd** ($D = 0.0451 \text{ cm}^{-1}$) and SnMe_3 in **Ve** ($D = 0.0450 \text{ cm}^{-1}$). They are only slightly better in delocalizing spin than the methyl derivative **Vc** ($D = 0.0456 \text{ cm}^{-1}$). These data are corroborated by Creary's results for the methylenecyclopropane rearrangement of *p*- SiMe_3 - and *p*- SnMe_3 -substituted derivatives.¹⁸ Unfortunately, no semiempirical parameters appear to be available for the Sn atom, such that the spin density for the allyl-radical fragment **Ae** could not be calculated. However, in view of the excellent correlation in Figure 2 for the large number of substituents presented therein, the spin density at the radical center for the SnMe_3 substituent may be estimated by extrapolation from the graph. Thus, from the experimental D value of 0.0450 cm^{-1} we determine for the SnMe_3 -substituted triplet diradical **Ve** a spin density of 0.540 at the allylic radical site, a value that is definitely lower than that of the parent allyl fragment **A_b** ($\rho = 0.573$). The D value for the SnMe_3

(14) Rauhut, G.; Chandrasekhar, J.; Alex, A.; Steinke, T.; Clark, T.; Sauer, W.; Beck, B.; Hutter, M.; Gedeck, P. *VAMP 6.1*; University of Erlangen-Nürnberg, 1996.

(15) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 764–766.

(16) Adam, W.; Kita, F.; Harrer, H. M.; Nau, W. M. *J. Org. Chem.* **1996**, *61*, 7056–7065.

(17) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 613–635.

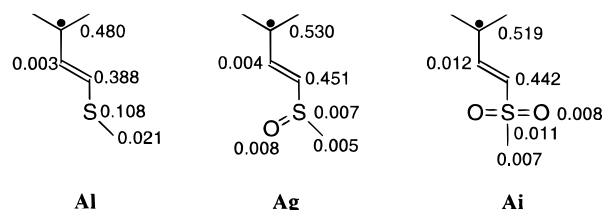
(18) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. J. *Org. Chem.* **1987**, *52*, 3254–3263.

substituent provides valuable experimental data to parametrize the tin atom for semiempirical methods.

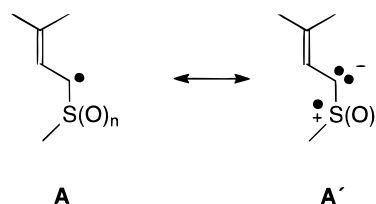
The D values for the halogen derivatives **Vf**, **Vh**, and **Vj** follow the order Cl (0.0437 cm^{-1}) < Br (0.0446 cm^{-1}) < I (0.0450 cm^{-1}), such that the chloro substituent delocalizes the spin best. Only a small heavy-atom effect is expected since the heavy atom acts predominantly on the spin-orbit coupling and not directly on the dipolar interaction.¹⁹ Compared to the large heavy-atom effects found for the 1,8-naphthodimethyl (0.0051 cm^{-1})^{20a} or the 2-methylene-1,3-cyclopentenediyl (ca. 0.2423 cm^{-1})^{20b} triplet diradicals, we estimate for the bromo-substituted triplet diradical **Vh** only about 0.0010 cm^{-1} and for the iodo **Vf** approximately 0.0024 cm^{-1} .²¹

As expected for the strongly radical-stabilizing ethoxy-carbonyl group in **Vk** ($D = 0.0413\text{ cm}^{-1}$), the cyano group in **Vm** ($D = 0.0400\text{ cm}^{-1}$), and the vinyl group in **Vp** ($D = 0.0333\text{ cm}^{-1}$), spin is efficiently delocalized into the allylic fragment by these substituents. Indeed, as the data in Table 1 reveal, the 1,3-butadienyl group in the triplet diradical **Vp** is just about the most effective π system for spin delocalization of the substituents investigated herein.

An informative set of vinyl-substituted **V** triplet diradicals in Table 1 is the sulfur-functionalized series **VI** ($D_{\text{SMe}} = 0.0407$), **Vg** ($D_{\text{SOMe}} = 0.0447$), and **Vi** ($D_{\text{SO}_2\text{Me}} = 0.0442$), which allows one to compare the efficacy of spin delocalization by the sulfanyl, sulfoxyl, and sulfonyl groups in the corresponding allylic species. Compared to the already discussed methoxy derivative **Va** ($D_{\text{OMe}} = 0.0480\text{ cm}^{-1}$), which localizes spin at the radical site, all of the sulfur substituents delocalize spin, and the order is MeS \gg MeSO₂ > MeSO. Actually, this is in qualitative accord with the α -hfc data of the corresponding XCH₂ radicals, for which the sequence SMe (1.65 mT) > SO₂Me (1.70 mT) > SOMe (1.99 mT) applies.²² The spin-density distributions for the corresponding allylic radical fragments **Ag**, **Ai**, and **Al** reproduce these electronic effects of the sulfur functionalities adequately. Thus, the spin density at the radical terminal without the X substituent is lowest for **Al** ($\rho_{\text{MeS}} = 0.480$) and highest for **Ag** ($\rho_{\text{MeOS}} = 0.530$), i.e., spin acceptance is most pronounced for the methylthio group. Correspondingly, the spin density at the sulfur atom is largest for **Al** ($\rho_{\text{SMe}} = 0.108$) and lowest for **Af** ($\rho_{\text{MeSO}} = 0.007$), but the latter is about the same magnitude as for **Ai** ($\rho_{\text{SO}_2\text{Me}} = 0.008$).



Qualitatively, the experimental D values of the triplet diradicals **Vg**, **Vi**, and **VI** and the theoretically assessed spin densities of the corresponding allylic radical fragments **Ag**, **Ai**, and **Al** may be rationalized in terms of the ease of the sulfur substituent to delocalize the spin from the adjacent radical site by the dipolar mesomeric structure in the resonance hybrid [**A** \leftrightarrow **A'**] given below.



The sulfanyl substituent (**Al**, $n = 0$) is clearly best in that it most effectively delocalizes spin onto the sulfur atom by donation of an electron to the allyl π system and the resulting positive charge is stabilized by the methyl group through hyperconjugation. For the sulfoxyl one (**Ag**, $n = 1$) such spin delocalization is less effective, while for the sulfonyl group (**Ai**, $n = 2$) it is not possible. The calculated spin densities at the sulfur atom in these functionalities nicely reproduce this trend, i.e., $\rho_{\text{SMe}} = 0.108$ in **Al**, $\rho_{\text{SOMe}} = 0.007$ in **Ag** and $\rho_{\text{SO}_2\text{Me}} = 0.008$ in **Ai**. Presumably, inductive effects play a role in why the sulfonyl group delocalizes spin slightly more effectively than the sulfoxyl one.

In summary, the present set of vinyl-substituted triplet diradicals **V** offer the following advantages in the investigation of electronic substituent properties at radical centers: (i) the aldehyde **2** serves as a convenient precursor for the essential vinyl-substituted azoalkanes **3**; (ii) a large variety of substituents may be connected to the radical site; and (iii) in the allylic fragment, the substituent effects are sufficiently amplified to assess accurately even small electronic effects of the substituent.

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Supporting Information Available: Synthetic details and characteristic spectral data of the azoalkanes **3** are presented. This material is available free of charge in the Internet under <http://www.pubs.acs.org>.

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(19) (a) Adam, W.; Fröhlich, L.; Nau, W. M.; Korth, H.-G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1339–1340. (b) Nau, W. M. Doctoral Dissertation, University of Würzburg, 1994.

(20) (a) Fritz, M. J.; Ramos, E. L.; Platz, M. S. *J. Org. Chem.* **1985**, *50*, 3522–3526. (b) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 151–194.

(21) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

(22) (a) Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1748–1752. (b) Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 908–912. (c) Davies, M. J.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 503–509.