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Spin Delocalization in 1-Heteroallyl Monoradicals as a Measure of Radical Stabilization by Heterovinyl Substituents Assessed through the EPR-Spectral Zero-Field *D* Parameter of 1,3-Cyclopentanediyl Triplet Diradicals

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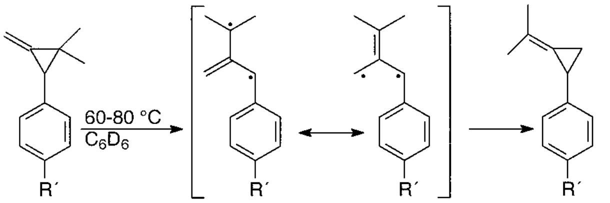
The EPR-spectral zero-field splitting parameter *D* of the localized heterovinyl-substituted 1,3-cyclopentanediyl triplet diradicals **T**, generated in a 2-methyltetrahydrofuran (MTHF) glass matrix at 77 K through the photochemical deazetation of the corresponding azoalkanes **1**−**13**, is a quantitative measure of the spin-density (ρ) variation by the substituents at the radical site in the 1-heteroallylic radicals. From these data, the radical-stabilizing ability of a variety of nitrogen-containing groups has been assessed, which includes imino and hydrazonyl functionalities. The radical stabilization in the heteroallylic radical fragment follows the order $X = O < NMe < CH_2 < CHMe \ll NOH \approx NOMe \ll NNHCHO \approx NNHC(O)NH_2 < NPh \approx NNMe_2 < NNH_2 < CHPh < NNHPh$. The lowest *D* values have been found for the hydrazonyl-substituted derivatives, which implies the lowest spin density at the carbon center and, thus, the most efficacious radical stabilization through spin delocalization. This *superdelocalization* may be rationalized in terms of nitrogen-centered radical-cationic structures. Localization of the spin at the terminal atom is resisted through the electronegativity effect (O < N < C).

Introduction

The electronic stabilization of allylic radicals by substituents is quite well understood,[1] whereas considerably less is known on the influence of terminal heteroatoms. In particular, of present interest is the effect of the nitrogen and oxygen atoms in the so-called 1-heteroallylic radicals ($C{=}C{-}X^{\bullet}$, $X = NR$ or O) on the spin-density (ρ) distribution and radical stabilization. Early theoretical work of Dannenberg and Tanaka on the coupling of the methyl radical with the simple 1-azaallyl radicals concluded that the attack at the carbon terminal is favored by 7.1 kcal/mol over that at the nitrogen site due to the higher spin concentration at the carbon center of the heteroallylic species.[2] These theoretical predictions on the 1-azaallyl radical were shortly afterward confirmed experimentally by MacInnes and Walton through α-hyperfine coupling constants, determined by EPR spectroscopy.[3] This EPR study was also substantiated theoretically, in which the rotation barriers of the carbon-centered versus the nitrogen-centered 1-azaallyl radical were calculated at the MNDO/3 level.[4] Rotation about the C−C bond is favored by about 1.9 kcal/mol over that about the C−N bond and, thus, less spin localization at the aza site. Most recently, an extensive study was conducted by the Creary and Engel groups, in which electronic substituent effects were assessed experimentally on the basis of chemical reactivity.[5] The rate constants (k_{rel}) for the thermal rearrangement of *para*-substituted 2-aryl-3,3-dimethylmethylidenecyclopropanes (Scheme 1), the basis of Creary's $\sigma^{\bullet}$ radical substituent [5]constants, were measured and the ability of various heterovinyl groups to stabilize a benzyl radical center was determined (Table 1). An unusually high radical stabilization for the hydrazonyl substituent was observed (last entry), for which the concept of *superdelocalization* was introduced.

Scheme 1. Rearrangement of *Para*-Substituted 2-Aryl-3,3-dimethylmethylidenecyclopropanes



Low-temperature persistent 1,3-cyclopentanediyl triplet diradicals **T** may be readily generated through the photochemical deazetation of diazabicyclo[2.2.1]heptene (DBH) derivatives[6] These triplet diradicals have been characterized by the zero-field-splitting (zfs) parameters

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(1) (a) Adam, W.; Emmert, O. *J. Org. Chem.* **2000**, *65*, 4127−4130. (b) Adam, W.; Emmert, O. *J. Org. Chem.* **2000**, *65*, 5664−5667. (c) Adam, W.; van Barnefeld, C.; Emmert, O. *J. Chem. Soc., Perkin Trans. 2* **2000**, *2*, 637−341.

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Table 1. Creary's Radical Substituent Constants ($\sigma^{\bullet}$) for the Thermal Rearrangement of 2-Aryl-3,3-dimethylcyclopropanes[a]

R′	k_{rel}	$\sigma^{\bullet}$ (Creary)
H	1.00	0.00
CH=N^{t}Bu	3.97	0.60
CH=CH$_2$	4.67	0.67
CH=NOH	5.08	0.71
CH=NOMe	5.60	0.71
CH=NNMe$_2$	8.27	0.92

[a] Reference 5.

D and *E*. For such localized triplet 1,3-diradicals **T**, the *D* parameter (the polar 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, as displayed in eq 1. The spin density as well as

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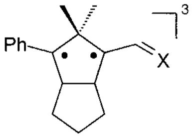
$$D = \frac{3\cdot\mu_0\cdot g_e^{2}\cdot\mu_B^{2}}{16\pi}\left(\frac{\rho_a\cdot\rho_b}{d_{ab}^{3}}\right)$$



T

(1)

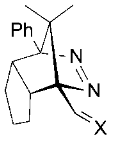
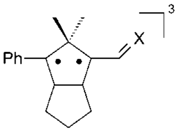
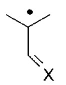
the distance dependences have been confirmed experimentally and theoretically,[7,8] which provide valuable structural and electronic information on radical species in question. When one radical site is kept electronically constant (e.g. phenyl substitution) at the radical site a, the *D* parameter is a sensitive probe of electronic substituents effect through the spin density ρ_b at the radical center b. This provides an accurate measure of radical stabilization in terms of the efficacy of spin delocalization in the monoradical fragment, in the present case the heteroallylic radical **M** in the triplet diradical **T**.

The incentive of the present study was to elucidate the electronic stabilization of a radical center by carbonyl, iminyl, and vinyl substituents. Herein we report the EPR-spectral data (*D* parameter) for the heterovinyl-substituted diradicals **T1**−**T13**, generated photochemically from the respective azoalkanes **1**−**13** (Table 2). From the *D* values we assess the electronic stabilization of the heteroallylic radical fragments **M1**−**M13** through the efficiency of spin delocalization by the heterovinyl substituent. The present results demonstrate unequivocally that the *D* parameter provides a reliable test of radical stabilization, as confirmed semiempirically by the PM3(AUHF)-calculated spin densities (ρ) and radical stabilization energies (RSE).

Results

For the synthesis of the desired imino-functionalized azoalkanes **2**, **5**−**11**, and **13**, the known azoaldehyde **1** was required. The latter was prepared by the established Hünig route[9] from the commercially available benzoylacetone in eight steps and an overall yield of 24%.[10] The condensation of the azoaldehyde **1** with a variety of amines, *N*-hydroxylamines, and hydrazines was carried out at ca. 20 °C, under the conditions specified in Table 3. The unknown bridgehead-substituted derivatives were isolated in good yields (71−98%) and have been fully characterized by their spectral and analytical data.

Table 2. Heterovinyl-Substituted Azoalkanes 1−13 as Photochemical Precursors to the Triplet Diradicals T with the Heteroallylic Monoradical Fragment M

X			
O	**1**	**T 1**	**M 1**
NMe	**2**	**T 2**	**M 2**
CH$_2$	**3**	**T 3**	**M 3**
CHMe	**4**	**T 4**	**M 4**
NOH	**5**	**T 5**	**M 5**
NOMe	**6**	**T 6**	**M 6**
NNHC(O)H	**7**	**T 7**	**M 7**
NNHC(O)NH$_2$	**8**	**T 8**	**M 8**
NPh	**9**	**T 9**	**M 9**
NNMe$_2$	**10**	**T 10**	**M 10**
NNH$_2$	**11**	**T 11**	**M 11**
CHPh	**12**	**T 12**	**M 12**
NNHPh	**13**	**T 13**	**M 13**

The triplet diradicals **T** were obtained by the direct irradiation of the corresponding azoalkanes in a 2-methyltetrahydrofuran matrix at 77 K with an argon-ion laser (364 nm). In all cases, the characteristic half-field signal ($\Delta m_s = \pm2$) for the triplet state is located at 1650−1680 G, the relevant diradical *z* signals ($\Delta m_s = \pm 1$) are $B_{min} = 1650 \pm 60$ and $B_{max} = 3924 \pm 60$ G at a microwave frequency of 9.43 GHz. The symmetry parameter (*E*) of the triplet diradicals is very small and, thus, the upper limit was estimated to be $E < 0.001$ cm^{-1}.

In Table 4 are listed the experimental *D* values for the nitrogen-functionalized triplet diradicals **T2**, **T5**−**11**, and **T13**, calculated from the EPR-spectral data. They have been arranged in order of decending values, i.e., in increasing degree of spin delocalization. For comparison purposes, also the oxygen-substituted (**T1**) and the carbon-substituted (**T3**, **T4**, and **T12**) congeners are given in Table 4, together with the theoretical spin densities (ρ) and the resonance stabilization energies (RSE) of the monoradical fragments **M**. For computational ease and convenience, these theoretical parameters were calculated for the corresponding heteroallyl radical fragments **M** in the triplet diradicals **T**.[11] The geometry optimization of the model monoradicals **M** was carried out by using the semiempirical PM3 method with annihilated UHF wave functions.[12] The spin densities (ρ) were determined by a single-point CI calculation to afford good $\langle S^2\rangle$ values between 0.752 and 0.761.[13]

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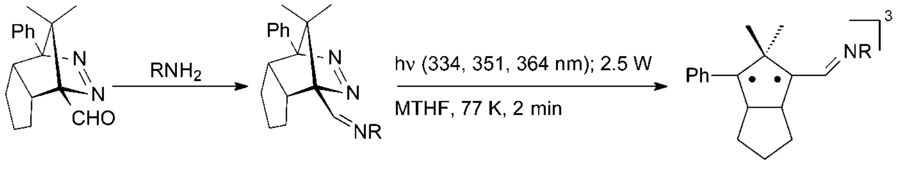
Table 3. Synthesis of the Azoalkanes 2, 5−11, and 13 and Their Corresponding Triplet Diradicals T2, T5−11, and T13

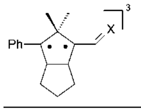
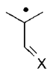


1 **2**, **5-11**, **13** **T2**, **T5-11**, **T13**

azoalkane	R	reagent	conditions[a] solvent/base/time	azoalkane yield [%]
2	Me	$MeNH_2 \cdot HCl$	ether/K_2CO_3/48 h	95
5	HO	$HONH_2 \cdot HCl$	MeOH/$NaHCO_3$/6 h	71
6	MeO	$MeONH_2 \cdot HCl$	MeOH/K_2CO_3/18 h	98
7	HC(O)NH	HC(O)NHNH$_2$	THF/48 h	92
8	$H_2NC(O)NH_2$	$NH_2C(O)NHNH_2 \cdot HCl$	MeOH/NaOAc/48 h	96
9	Ph	$PhNH_2$	THF/40 h	80
10	Me_2N	Me_2NNH_2	THF/6 h	90
11	H_2N	N_2H_4	THF/18 h	95
13	PhNH	$PhNHNH_2$	THF/2 h	97

[a] The condensations were carried out at ca. 20 °C.

Table 4. Experimental Zero-Field EPR *D* Parameter of the Matrix-Isolated Triplet Diradicals T1−13 and the Semiempirically Calculated Spin Densities (*ρ*) of the Respective Monoradicals Fragments M1-13

		X	$\lvert D/hc \rvert$[a]	ρ_α[b]	RSE[c]
T 1	**M 1**	O	0.0535[d]	0.764	1.76
T 2	**M 2**	NMe	0.0496	0.612	4.57
T 3	**M 3**	CH_2	0.0473[e]	0.591	4.68
T 4	**M 4**	CHMe	0.0456[e]	0.517	5.23
T 5	**M 5**	NOH	0.0441	0.554	6.32
T 6	**M 6**	NOMe	0.0440	0.520	6.81
T 7	**M 7**	NNHC(O)H	0.0413	0.396	7.51
T 8	**M 8**	NNHC(O)NH$_2$	0.0410	0.403	7.49
T 9	**M 9**	NPh	0.0405	0.403	8.04
T10	**M10**	$NNMe_2$	0.0400	0.356	7.19
T11	**M11**	NNH_2	0.0393	0.379	8.00
T12	**M12**	CHPh	0.0357[e]	0.339	8.64
T13	**M13**	NNHPh	0.0350	0.257	9.35

[a] Recorded at 77 K in a 2-methyltetrahydrofuran (MTHF) matrix, values given in cm^{-1}, accuracy ± 0.0001 cm^{-1}. [b] Computed for the monoradical fragments **M** with the semiempirical AUHF/PM3 method. [c] RSE as a difference of the $\Delta H_f°$ between the 0° and the 90° AUHF/PM3-computed conformers, values given in kcal/mol. [d] Experimental data taken from ref 11. [e] Experimental data taken from ref 1a.

The theoretical spin densities (*ρ*) at the radical site are related to the experimental *D* value by eq 1, which allows to assess the efficiency of the spin delocalization by the heterovinyl substituents in the triplet diradicals **T**. Clearly, the formyl functionality in **T1** is the least, the *N*-phenylhydrazonyl group in **T13** the most effective in the spin delocalization in these triplet diradicals. The ability of the vinyl-substituted derivatives **T3**, **T4**, and **T12** to stabilize the radical center falls between these two heterovinyl-substituted (C═O and C═NX) extremes.

Discussion

We assume that all diradicals **T1**−**T13** possess planar geometries, as borne out by the MO calculations (PM3 method),[13] which yield an energy minimum for the planar 1,3-cyclopentanediyl ring with coplanar substituents at the radical sites. 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] triplet diradicals. According to semiempirical computations (AM1 method), the rotation of the substituents in the diradical requires an appreciable activation barrier (7 kcal/mol).[16] Therefore, the observed changes in the *D* values reflect the electronic effects exerted by the substituents on the spin delocalization in the planar triplet diradicals **T**.[16]

Since in all the present unsymmetrical derivatives **T1**−**T13** one radical center is kept "electronically" constant (phenyl substitution), the experimentally assessed changes in the *D* parameter provide a measure of the efficacy of delocalization by the heterovinylic substituent on the other radical site. According to eq 1, the *D* value depends on the spin density (*ρ*) at this radical site and relates the experimental *D* values of the triplet diradical **T** to the theoretically accessible spin densities of the monoradicals **M**. Therewith, the opportunity is provided to evaluate quantitatively the observed electronic substituent effects.

Indeed, as displayed in Figure 1, the experimental *D* values of the triplet diradicals **T** correlate impressively well ($r^2 = 0.950$, $n = 13$) with the calculated spin densities (*ρ*) of the monoradical fragments **M**. Thus, the lower the *D* value, the less the spin density at the radical center, the higher the delocalization by the heterovinylic substituent and, consequently, the better stabilized the radical system.

The latter trend may be tested quantitatively by the so-called radical stabilization energy (RSE),[17] as shown in Figure 2. The RSE may be conveniently computed from the difference between the enthalpies of formation ($\Delta H_f°$) of the 90° (no delocalization) and the 0° (maximum of

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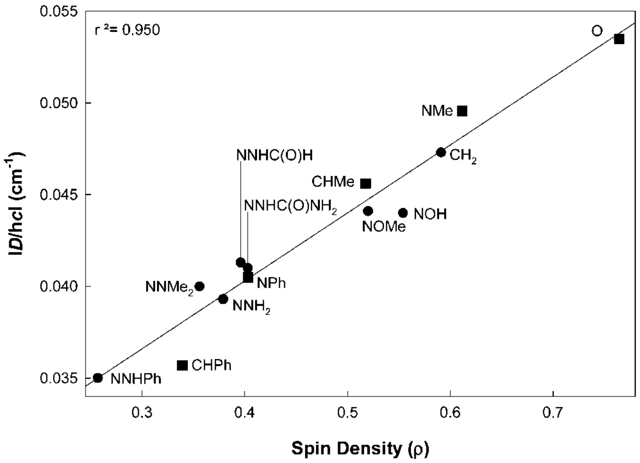


Figure 1. Experimental D parameter of the triplet diradicals **T1**−**13** versus the PM3-calculated spin densities of the corresponding monoradical fragments **M1**−**13**.

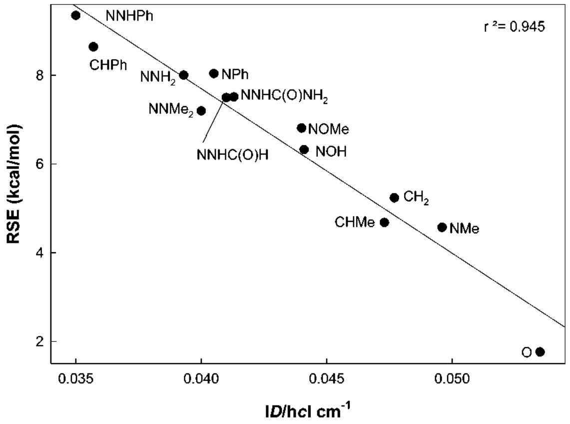
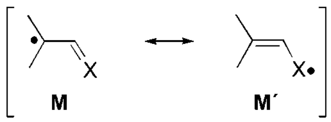


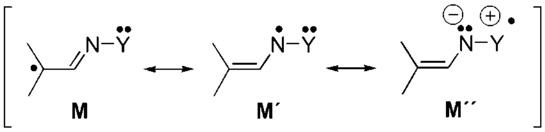
Figure 2. Correlation of the AUHF/PM3-calculated RSE of the monoradical fragments **M** versus the D parameter of the triplet diradicals **T**.

delocalization) conformers by the semiempirical AUHF/PM3 method. The good correlation ($r^2 = 0.945$, $n = 13$) between the calculated RSE values of the triplet diradicals **T** and the experimentally determined D values unmistakenly demonstrates that the electronic stabilization effects in the 1-heteroallyl radicals are reliably assessed by the D parameter of the corresponding triplet diradicals.

It now remains to examine the delocalizing propensity of particular sets of heterovinylic substituents in Table 2 and rationalize the observed trends. An informative set constitutes the variation of the terminal atom (X = O, N, C) of the heteroallylic radical fragment **M** in the triplet diradical **T**, to assess how effective the heteroatom is in acquiring the unpaired electron, i.e., the mesomeric structure **M′**. The pertinent derivatives are the triplet diradicals **T1** (X = O), **T2**, **9** (X = NMe, NPh) and **T4**, **12** (X = CHMe, CHPh), which are denoted by the filled squares in Figure 1. Clearly, the overriding electronic effect is the electronegativity of the terminal atom (O > N > C), which resists acquisition of the unpaired electron (mesomeric structure **M′**), as perfectly displayed by the observed D values (Table 2) for the cases **T1** (X = O) > **T2** (X = NMe) > **T4** (X = CHMe). Thus, the formyl group in **T1** (X = O) is the worst substituent for electron delocalization, the imino group in **T2** (X = NMe) is intermediate, and the vinyl one in **T4** (X = CHMe) is the most effective. The same trend in electron delocalization is also displayed by the phenyl derivatives **T9** (X = NPh) and **T12** (X = CHPh), which both efficiently stabilize the X radical site, but the styryl group in **T12** (X = CHPh) is considerably better than the phenylimino substituent in **T9** (X = NPh).



The other revealing set on electronic stabilization through delocalization in heteroallylic radicals are the derivatives in which the doubly bonded nitrogen atom bears another heteroatom. These are the oxime derivatives **T5** (X = NOH) and **T6** (X = NOMe), as well as the hydrazone derivatives **T10** (X = $NNMe_2$), **T11** (X = NH_2), and **T13** (X = NNHPh). The electronegativity effect is again evident, in that the oximes **T5** and **T6** are less effective in delocalizing the spin density compared to the hydrazones **T10**, **T11**, and **T13**. Nevertheless, both oxime derivatives **T5** (X = NOH) and **T6** (X = NOMe) are slightly better in delocalizing spin in the heteroallyl radical than the imine **T2** (X = NMe), as evidenced by both the experimental D values and the computed ρ spin densities (Table 2). Presumably, the α heteroatom additionally affects electron delocalization through the mesomeric structures **M″** shown below. Again, the oxygen functionalities (Y = O) in the oxime derivatives **T5** (X = N−OH) and **T6** (X = N−OMe) are less prone to acquire the positive charge than the nitrogen functionality in the hydrazone derivatives **T10** (X = $NNMe_2$), **T11** (X = NH_2), and **T13** (X = NNHPh). In fact, the phenylhydrazone **T13** (X = NNPh) is the best in stabilizing the radical center, since it has the lowest D value of all the cases in Table 2 and, thus, the lowest spin density (ρ) at the radical center. Clearly, the phenyl substituent of the hydrazone functionality in the **T13** (X = NNHPh) case provides for further delocalization, analogous to the imine **T9** (X = NPh) of the previously discussed set. In contrast, when the hydrazone functionality bears electron acceptors such as the formyl group in **T7** (X = NNHC(O)H) or the carboxamide group in **T8** (X = $NNHC(O)NH_2$), spin delocalization is diminished (Table 2) through depreciation of the mesomeric structure **M″**.



The superdelocalizing ability of the hydrazonyl functionality on a radical center, as in the **T11** (X = NNH_2) derivative, has been recognized previously by Creary and Engel groups in the thermal rearrangement of 2-aryl-3,3-dimethylenecyclopropanes.[5] A number of related heteroallylic radicals had been examined to assess their radical-stabilizing propensity on the basis of such chemical-reactivity methods, and the $\sigma^{\bullet}$ constants of these substituents were determined. The correlation between our D values (an EPR-spectral quantity) of the triplet diradicals **T** and the $\sigma^{\bullet}$ values (a kinetic quantity based

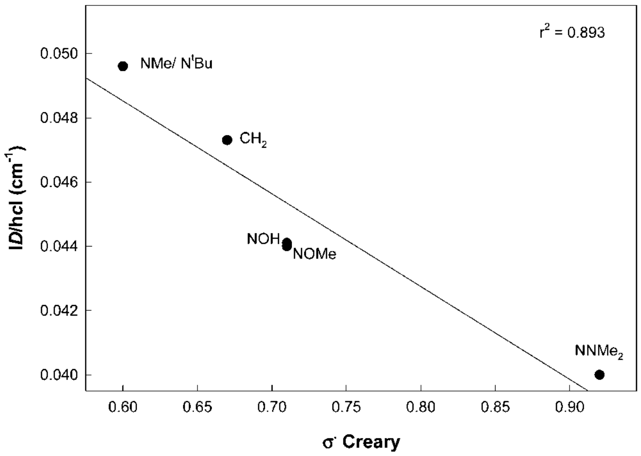


Figure 3. Correlation between the EPR-spectral *D* values of the triplet diradicals **T** and the kinetic $\sigma^{\bullet}$ values of corresponding heteroaryl substituents.

on chemical reactivity) for corresponding heterovinylic groups is fair ($r^2 = 0.893$) as displayed in Figure 3.

The deviations presumably arise through polar contributions (σ_p values)[18] in the chemical-reactivity scale ($\sigma^{\bullet}$ values), as pointed out previously for a similar correlation of electronic substituent effects in radicals.[16] Unfortunately, only a few of the σ_p values are available[18] for this set of substituents, such that it was not feasible to carry out the corrections for possible polar effects.

Conclusion

The spin delocalization by a variety of substituents in a set of 1-heteroallylic monoradicals **M** may be conveniently determined from the EPR-spectral *D* parameter of the corresponding 1,3-cyclopentanediyl triplet diradicals **T**. This method provides a reliable measure of radical stabilization in heterosubstituted species, as confirmed by semiempirical [PM3(AUHF)] calculations of the spin densities (ρ) and radical stabilization energies (RSE), which are in good accord ($r^2 = 0.950$) with the experimental *D* values. A fair ($r^2 = 0.893$) correlation has been obtained with Creary's kinetically determined radical substituent constants ($\sigma^{\bullet}$ values). The efficient spin delocalization and, consequently, radical stabilization of the allylic system is significantly reduced by the terminal substituent, the observed O > N > C order in the series **M1**, **M2**, and **M3** is in line with the expected electronegativity effect. In contrast, α-heteroatom substitution, as in the hydrazonyl radical **M13**, promotes superdelocalization through mesomeric radical-cationic structures **M″**.

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Supporting Information Available: Synthetic details and spectral data of the azoalkanes **2**, **5**−**11**, and **13** are presented. This material is avaliable free of charge via the Internet at http://www.pubs.acs.org.

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(18) Hansch, C.; Leo, A.; Winfeld, A. L.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.