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Electronic Effects of *para*- and *meta*-Substituents on the EPR *D* Parameter in 1,3-Arylcyclopentane-1,3-diyl Triplet Diradicals. A New Spectroscopic Measure of α Spin Densities and Radical Stabilization Energies in Benzyl-Type Monoradicals

Waldemar Adam,*[,†] Heinrich M. Harrer,[†] Fumio Kita,[†] Hans-Gert Korth,[‡] and
Werner M. Nau[†]

*Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, and
Universität-Gesamthochschule Essen, Universitätsstrasse 5, D-45117 Essen, Germany*

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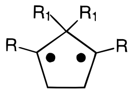
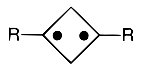
The zero-field splitting *D* parameter was determined in a 2-MTHF glass matrix at 77 K for a large set (35 derivatives) of *para*- and *meta*-substituted 1,3-arylcyclopentane-1,3-diyl *triplet diradicals* **6**. The *D* values are a sensitive function of electronic substituent effects; for convenience, the ΔD scale was defined as the difference $D_H - D_X$. Spin acceptors decrease while spin donors increase the *D* value relative to the unsubstituted reference system (D_H). Theoretical (PM3-AUHF) α spin densities (ρ_α) for the corresponding cumyl monoradicals **7** display a good linear dependence ($r^2 = 0.963$) when plotted against the *D* parameters of the *triplet diradicals* **6**. The radical stabilization energies (RSE) of the cumyl radicals **7** were semiempirically calculated as the energy difference between in-plane (full conjugation) and perpendicular (no conjugation) conformations of the aryl groups and shown to correlate linearly ($r^2 = 0.947$) against the experimental *D* parameter for the corresponding *triplet diradicals* **6**. These linear correlations, i.e., *D versus* ρ_α and *versus* RSE, demonstrate that the *D* parameter of the localized *triplet diradicals* **6** reflects reliably electronic substituent effects in benzyl-type monoradicals. The spectroscopic ΔD scale correlates poorly with the reported chemical σ_{rad} scales, unless polar corrections (Hammett σ_{pol} values) are made by means of a two-parameter Hammett treatment. Then a good linear correlation ($r^2 = 0.921$) of the ΔD values *versus* the Creary σ_{rad} scale applies; as expected, the radical effects dominate ($\rho_{rad} = 1.00$ *versus* $\rho_{pol} = 0.41$). The advantages of the new EPR-spectroscopic ΔD scale are that polar effects are nominal and the *D* parameter can be measured experimentally with sufficient accuracy to probe even small and subtle electronic effects through changes in the α spin densities.

Introduction

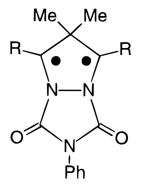
Systems with triplet spin multiplicity can be characterized by low-temperature matrix EPR spectroscopy[1] by means of the zero-field splitting parameters *D* and *E*, which provide valuable information on the electronic properties of these paramagnetic species.[2] Dipolar spin−spin interactions are expected to be the dominant contributions in localized *triplet diradicals*, in which the radical centers are not joined through a π system and the changes in their *D* parameters with electronic structure should be well predictable by the dipole approximation ($D \propto 1/r^3$).[2,3] Prototypes of this class and excellent test cases of the dipole approximation are the triplet 1,3-cyclopentanediyl[4,5] and 1,3-cyclobutanediyl[6] diradicals **1** and **2**. Arnold's urazole-substituted 1,3-diradicals **3**[7ab] and **4**[7c] have provided the earliest triplet EPR spectra. The work by Closs on the parent 1,3-cyclopentanediyl diradical **1a**[4] has become a seminal study in this field, while Dougherty's thorough work[6] on the substituted cyclobutane-1,3-diyl diradicals **2** constitutes a significant advance.



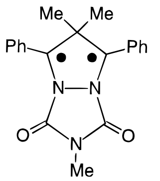
1a (R = R1 = H)
1b (R = Ph; R1 = H)
1c (R = Ph; R1 = Me)



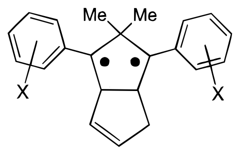
2
(R = Me, Et, Ph, Vin)



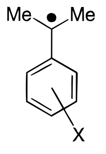
3
(R = Me, Ph)



4



6



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Dougherty's anticipation[6] that no special electronic effects (captodative stabilization, spin polarization, etc.) should play a significant role in *triplet 1,3-diradicals* was recently confirmed experimentally and theoretically for

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[†] Universität Würzburg.

[‡] Universität-Gesamthochschule Essen.

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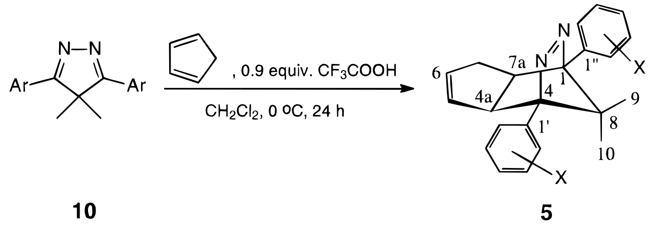
the bicyclic 1,3-cyclopentanediyl diradical derivatives **6**.[8b,c] As a consequence, such 1,3-diaryl-substituted cyclopentane-1,3-diyl *triplet diradicals* can be described as a composite of two cumyl radical fragments **7**, which may provide the opportunity to assess electronic substituent effects on benzyl-type monoradicals through the EPR *D* parameter of the corresponding *triplet diradicals*. This was demonstrated by a direct linear dependence between the *D* parameters of such *triplet diradicals* and the a_β hyperfine splitting constants of the corresponding cumyl monoradicals in terms of substituent effects.[8b,c]

Electronic substituent effects on the benzyl-type radicals are quantitatively assessed with the help of the Hammett treatment, and to date, five σ_{rad} scales are available of which four are kinetic ones. For example, the Fisher scale[9] is based on the *N*-bromosuccinimide-initiated hydrogen abstraction from aryl-substituted *m*-cyanotoluenes. The most comprehensive kinetic scale is that by Creary,[10] which was derived from the relative rearrangement rates of 2-aryl-3,3-dimethylmethylenecyclopropanes. For the Jackson scale,[11] the thermolysis of dibenzylmercury compounds was employed. The most recent kinetic scale comes from Jiang,[12] who applied the dimerization rates of substituted trifluorostyrenes for this purpose. The fifth scale, proposed by Arnold,[13a] is based on EPR-spectral properties, namely the α hydrogen hyperfine splitting constants (a_α) of substituted benzyl radicals. A similar scale was developed for the *para*-hydrogen and *p*-methyl hyperfine splitting constants of α-substituted benzyl radicals.[13b,c]

Unfortunately, these different σ_{rad} scales suffer from various shortcomings. For example, steric repulsion of large substituents at the *para* position by the *m*-cyano substituent are expected to present problems in the Fisher scale.[9b] Also, preparative problems for interesting substituents are encountered,[10,13a] which is especially the case for the Jackson scale and seriously restricts the available range of substituents. Moreover, the assumption that *meta* substituents have no effect on the radical stability of the intermediate benzyl-type radicals has been seriously questioned.[9b,10a,13a] In Jiang's scale,[12a,b] the σ_{rad} values had to be recalibrated with a tailor-made polar substituent constant σ_{mb}. It is such polar contributions in the transition state as well as on the ground state that encumber the reliable assessment of substituent effects in the kinetic σ_{rad} scales. For example, we have recently demonstrated[14] that the thermolysis of azoalkanes, which was long believed to be a reaction with *true radical character*, is strongly influenced by polar effects. Hence, no data are accessible for radical species that can be directly related to the radical stabilization energies (RSE) of the substituents. For this reason, it appears that Arnold's EPR spectroscopic scale should be the most suitable one to adequately reflect substituent effects in benzyl radicals since it measures the changes of the α hyperfine splitting constants of the free radicals as a function of the substituent. Unfortunately, the σ_α scale does not provide data for such important substituents as NO_2 or NR_2 on account of generating such benzyl radicals in solution.

Scheme 1



It should be evident that a number of criteria are important in choosing a model system for evaluating substituent effects on radical species:[11a] (1) there should be a direct interaction between the substituent and the radical site, (2) the mechanism of the reaction should be well understood, (3) side reactions should be minimized, (4) the substituent effect should be sufficiently large to be accurately determinable, (5) polar effects should be minimal, (6) a wide range of substituents should be featured, i.e., at least *p*-OMe, *m*-Me, H, *p*-Cl, *m*-Cl, *p*-NO_2, and *m*-NO_2,[15] (7) solvent and steric effects should be negligible, and (8) the model compounds should be readily accessible.

Presently, we report our results on the experimental *D* parameters of the symmetrically *para*- and *meta*-substituted 1,3-diarylcyclopentane-1,3-diyl *triplet diradicals* **6**, which as model system cover most of the mentioned prerequisites. These data form the basis for a new spectroscopic scale to evaluate electronic substituent effects in benzyl-type radicals in terms of the Δ*D* parameter (eq 1).[8]

$$\Delta D = (D_{\mathrm{H}} - D_{\mathrm{X}})/hc \tag{1}$$

A comparison is made with other σ_{rad} scales for benzyl-type monoradicals. We will show that the *D* parameter of the *triplet diradicals* **6** serves as a quantitative measure of α spin density (ρ_α) in the cumyl monoradicals **7**, which can be obtained by semiempirical MO calculations. Finally, the electronic substituent effects on *triplet diradicals* provide a direct measure of radical stabilization energies (RSE).

Results

Syntheses. The azoalkanes **5** were prepared through the acid-catalyzed cycloaddition of the corresponding 4,4-dimethyl-3,5-diaryl-4*H*-pyrazoles with cyclopentadiene (Scheme 1).[14,16] This pathway was not successful for the azoalkanes **5p** (X = OH) due to the poor solubility of the

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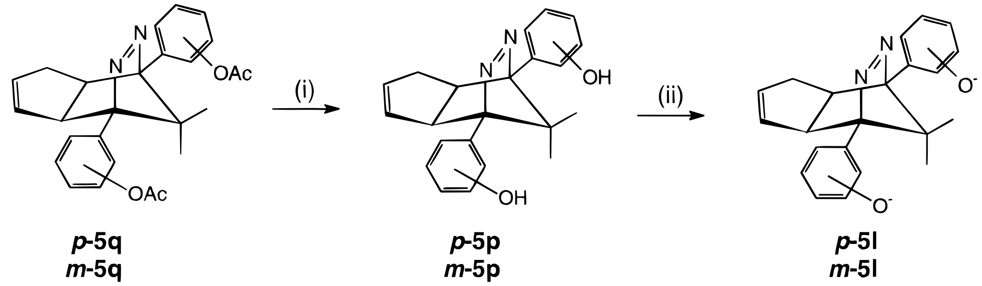
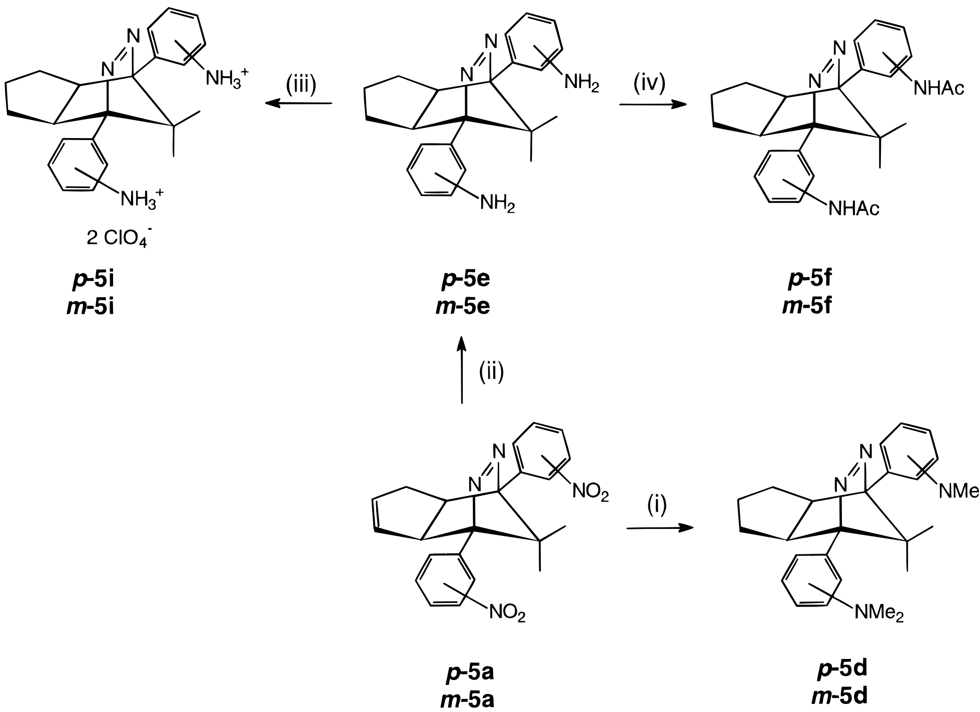
Scheme 2[a]



[a] Key: (i) $N_2H_4 \cdot H_2O$, CH_2Cl_2, reflux, 3 h; (ii) dry pyridine (5 equiv), 2-MTHF.

Scheme 3[a]



[a] Key: (i) CH_2O (2 equiv), PtO_2, H_2, EtOH, ca. 20 °C, 36 h; (ii) Pd/C, H_2, EtOAc/EtOH (1:1), ca. 20 °C, 48 h; (iii) 70% $HClO_4$ (2 equiv), methyl *tert*-butyl ether, ca. 20 °C, 20 min; (iv) Ac_2O (2 equiv), CH_2Cl_2, reflux, 4 h.

corresponding 4*H*-pyrazoles. These derivatives were synthesized by saponification of the azoalkanes **5q** (X = OCOMe) with hydrazine hydrate. The azoalkanes **5l** (X = O^-) were generated *in situ* by addition of a molar excess of pyridine base to a solution of the corresponding hydroxy-substituted azoalkanes **5p** (Scheme 2).

A convenient procedure for the synthesis of the dimethylamino derivatives **5d** was developed by reductive alkylation of the corresponding nitro derivatives **5a** with formaldehyde (Scheme 3). The azoalkanes **5i** (X = NH_3^+) were obtained in high yields by protonation with 70% perchloric acid of the amino-substituted azoalkanes **5e**. The latter ones were conveniently accessible through catalytic hydrogenation (palladium-charcoal) of the corresponding nitro-substituted azoalkanes **5a**. The *N*-acylated derivatives **5f** were prepared from the azoalkanes **5e** by treatment with acetic anhydride in boiling dichloromethane (Scheme 3).

EPR Spectroscopy. The diradicals **6** were obtained by direct irradiation of the corresponding azoalkanes **5** in 2-methyltetrahydrofuran (MTHF) glass at 77 K by means of a mercury/xenon high-pressure lamp (320−400 nm) or an argon ion laser (364 nm). The triplet diradicals **6** are the most persistent localized diradicals known to date, as manifested by the constant signal intensity even after 2 h at 77 K. In one case,[17] the half-life was accurately determined and found to be 30 h at 77 K. In all cases, the EPR half-field signal ($\Delta m_s = \pm 2$), characteristic for triplet states,[2,3] was located at 1650−1680 G, whereas the relevant diradical signals in the $\Delta m_s = \pm 1$ region were located at $B_{min} = 2841 \pm 30$ G and $B_{max} = 3924 \pm 30$ G at a microwave frequency of 9.4 GHz. Table 1 reveals for the triplet diradicals **6** a significant dependence of the zero-field splitting parameter *D* on the electronic nature of the aryl substituents. The *E* parameter of the *triplet diradicals* **6** was very small in all cases, and thus, only an upper limit (≤ 0.001 cm^{-1}) can be given. The EPR half-field signals ($\Delta m_s = \pm 2$) of the *triplet diradicals* **6** showed hyperfine splitting in most cases. The largest coupling of 9−10 G was assigned to the hyperfine coupling with the hydrogen atoms of the β ethano bridge. Further unresolved fine structure and signal broadening may derive from hyperfine coupling with the *ortho*- and *meta*-hydrogen atoms of the aromatic moiety. A simulation of the half-field signal for the *triplet diradical* ***p*-6o** is available as Supporting Information.

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Table 1. Zero-Field Splitting Parameters *D* of the Triplet Diradicals 6[a] and Calculated α Spin Densities (PM3-AUHF) of the Cumyl Radicals 7

	para-X	$\lvert D/hc\rvert 10^2$ [b]	ρ_α [c]		*meta*-X	$\lvert D/hc\rvert 10^2$ [b]	ρ_α [c]
***p*-6a**	*p*-NO_2[d]	4.14	0.492	***m*-6a**	*m*-NO_2	5.10	0.543
***p*-6b**	*p*-CN	4.50	0.513	***m*-6b**	*m*-CN	5.18	0.545
***p*-6c**	*p*-CO_2Me	4.51	0.513				
***p*-6d**	*p*-NMe_2[e]	4.74	0.520	***m*-6d**	*m*-NMe_2[e]	5.28	0.553
***p*-6e**	*p*-NH_2[e]	4.76	0.521	***m*-6e**	*m*-NH_2[e]	5.23	0.552
***p*-6f**	*p*-NHCOMe	4.84	0.526	***m*-6f**	*m*-NHCOMe[e]	5.20	0.548
***p*-6g**	*p*-CF_3	4.93	0.529	***m*-6g**	*m*-CF_3	5.04	0.542
***p*-6h**	*p*-Cl[d]	4.95	0.529	***m*-6h**	*m*-Cl	5.12	0.544
***p*-6i**	*p*-NH_3^+	4.98	*f*	**m-6i**	m-NH_3^+	5.17	*f*
***p*-6j**	*p*-Br[d]	5.00	0.539				
***p*-6k**	*p*-I	5.00	0.536	***m*-6k**	*m*-I	5.13	0.548
***p*-6l**	*p*-O^-	5.02	*f*	***m*-6l**	*m*-O^-	5.23	*f*
***p*-6m**	*p*-Me[d]	5.02	0.539	***m*-6m**	*m*-Me	5.14	0.545
***p*-6n**	**H**[d]	**5.04**	**0.542**	***m*-6n**	**H**[d]	**5.04**	**0.542**
***p*-6o**	*p*-OMe[d]	5.09	0.536	***m*-6o**	*m*-OMe	5.19	0.550
***p*-6p**	*p*-OH	5.09	0.537	***m*-6p**	*m*-OH	5.26	0.552
***p*-6q**	*p*-OCOMe	5.15	0.542	***m*-6q**	*m*-OCOMe	5.14	0.547
***p*-6r**	*p*-F[d]	5.21	0.532[f]	***m*-6r**	*m*-F	5.17	0.547
				***m*-6s**	*m*-CH_2CH_2Ph[e]	5.13	0.544
				***m*-6t**	*m*-C≡CPh	5.29	0.551

[a] Measured in a MTHF glass matrix at 77 K, for all triplet diradicals **6** $\lvert E/hc\rvert < 0.001$ cm^{-1}. [b] Values given in cm^{-1}, error $\pm$ 0.01 × 10^2 cm^{-1}. [c] ρ_α is defined as the square of the SOMO p_z coefficient of the α carbon in the cumyl radicals **7**. [d] Reference 8a. [e] Hydrogenated derivatives, *D* value 0.0506 cm^{-1} for the reference system (*para*-H). [f] Computed values too low, *cf.* text.

Discussion

Structural Aspects of the Cyclopentane-1,3-diyl Triplet Diradicals 6. We assume that all diradicals **6** possess the same geometry, as is borne out by MO calculations (AM1),[18] which yield a distinct energy minimum for a planar 1,3-cylopentanediyl moiety with coplanar aryl groups. The planarity of the 1,3-cyclopentanediyl moiety is in line with earlier *ab initio* calculations for the planar 1,3-cyclobutanediyl[19] and the parent 1,3-cyclopentanediyl[20] diradicals. Besides, the coplanar arrangement of the aryl groups allows for the maximum contribution of the benzylic resonance stabilization, which is worth ca. 12−13 kcal/mol for the corresponding monoradicals.[13a,21] According to the semiempirical AM1 method, twisting of the aryl groups in the diradicals **6** requires an appreciable activation barrier (7 kcal/mol) at 77 K. Therefore, the observed changes in the *D* values are proposed to represent electronic effects by the aryl substituents on the spin delocalization in the benzyl radical moiety rather than variations in the conformational features of the *triplet diradicals*.

Spin Density Dependence. It was recently demonstrated that a direct dependence exists between the *D* parameter of the localized cyclopentane-1,3-diyl *triplet diradicals* **6** and the spin densities ρ_A and ρ_B at the radical termini A and B with d_{AB} as the distance between the A and B spin sites (eq 2).[8b,c] Hence, this relationship

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

offers the opportunity to link the experimental *D* values of the *triplet diradicals* **6** to the theoretically accessible spin densities of cumyl monoradicals **7** and evaluate thereby quantitatively electronic substituent effects. However, it is known that semiempirical and *ab initio* MO calculations for the benzyl[22] and the cumyl[23] radicals suffer from severe spin contamination due to higher spin states, which exaggerate the expected $\langle S^2\rangle$ value of 0.75 for a pure doublet state up to as much as 1.3. Therefore, for the geometry optimization of the model cumyl radicals **7** the annihilated UHF wave function[24] within the PM3 method[25] was employed, which gave for *all* calculated cumyl radicals $\langle S^2\rangle = 0.750$. The α spin densities ρ_α (the square of the SOMO p_z orbital coefficient of the α carbon) were then determined by a single-point CI calculation to give acceptable $\langle S^2\rangle$ values between 0.76 and 0.78. With this procedure, the α:*ortho*:*para* spin density distribution for the parent cumyl radical (X = H) was calculated to be 0.542:0.121:0.123, which is in quite good agreement with the experimentally derived spin density distribution 0.587:0.169:0.200.[8c,13] Moreover, a quite good correlation ($a_\beta = 30.73\rho_\alpha - 0.36$, $r = 0.940$; $n = 10$) was found for the calculated α spin densities of the *para*-substituted cumyl radicals **7** against their corresponding a_β hyperfine splitting constants.[13] Thus, with this semiempirical method the α spin densities are estimated as satisfactorily as with the more sophisticated BLYP/6-31G* density functional method employed recently for the a_α hyperfine splitting constants of substituted benzyl radicals ($a_\alpha = 19.68\rho_\alpha + 3.71$, $r = 0.941$; $n = 12$).[12c]

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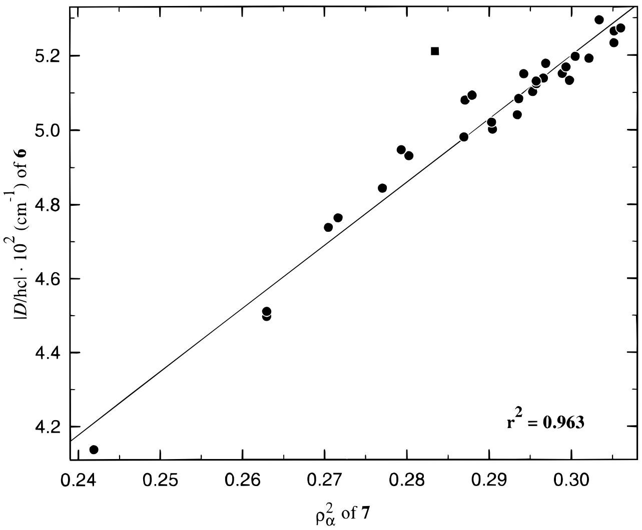

Figure 1. Experimental D parameters of the *triplet diradicals* **6** *versus* the square of the calculated (PM3-AUHF) α spin density (ρ_α) of the cumyl monoradical fragments **7**: (■) p-F substituent (*cf.* text).

As displayed in Figure 1, the D parameters of the *triplet diradicals* **6** are linearly dependent ($|D/hc|100 = 17.04\rho_\alpha^2 + 0.1$; $r^2 = 0.963$; $n = 30$) on the square (*cf.* eq 2) of the calculated ρ_α values of the corresponding cumyl monoradicals **7**. As expected, through the delocalization propensity of the substituents, the ρ_α and, thus, the D values are decreased relative to the parent system (X = H) for strong spin-accepting groups ($\Delta D > 0$) such as p-NO_2, p-CN, p-NH_2, and p-NMe_2. Interestingly, our results show unequivocally that all *meta* substituents, electron-accepting as well as electron-donating ones, increase the ρ_α and the D values substantially with respect to the unsubstituted derivative (X = H); this happenstance qualifies them as spin-donating groups ($\Delta D < 0$). The only substituent that deviates strongly from this linear correlation is p-F, but this substituent notoriously presents difficulties in such MO calculations. Similar problems were found for the charged derivatives X = p-NH_3^+, m-NH_3^+, p-O^-, and m-O^-; therefore, these values were not considered in the correlation. Nevertheless, the linear correspondence between the experimental D values of the *para*- and *meta*-substituted localized *triplet 1,3-diradicals* **6** and the theoretical ρ_α values of the cumyl monoradicals **7** (Figure 1) provides strong evidence that electronic substituent effects are realistically assessed. *Thus, we contend that triplet diradicals are a reliable monitor of electron delocalization in benzyl-type monoradicals.*

Radical Stabilization Energies. The delocalization of the unpaired electron in radicals provides stabilization, and such substituent effects have been quantitatively assessed in terms of the so-called radical stabilization energy (RSE). For benzyl (or cumyl) radicals, the RSE values can be estimated from the rotational barriers of the terminal methylene (or isopropylidene group) around the CC bond, a process that disrupts π conjugation.[13a,22b,e] Such RSE values may be conveniently determined by computing such barriers as the differene (eq 3) between

$$\mathrm{RSE} = \Delta H_f(90°) - \Delta H_f(0°) \qquad (3)$$

the energy of the 90° conformation (no delocalization) and the 0° conformation (maximal delocalization). These computations were performed in the same manner[24,25] as

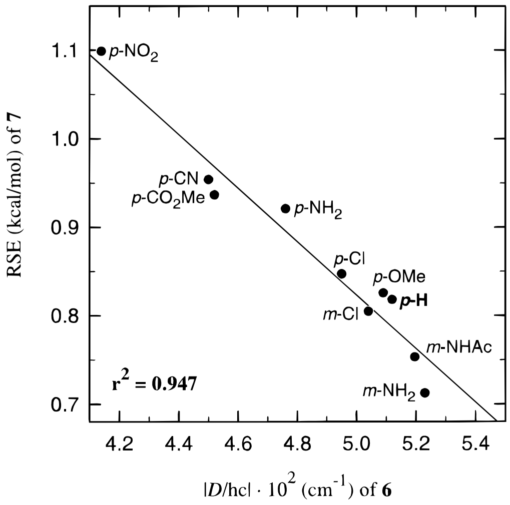

Figure 2. Calculated RSE values of the cumyl radicals **7** *versus* the D values of the *triplet diradicals* **6**.

described for the α spin density (*vide supra*) on a selected set of substituents, but the full range of substituent effects was spanned, e.g., NO_2 through NH_2. A good dependence was found between the calculated RSE values for the cumyl monoradicals **7** and the experimental D parameters of the *triplet diradicals* **6** (Figure 2; $r^2 = 0.947$, $n = 10$). However, the calculated RSE differences for the substituents are relatively small and cover a range from only 0.7 to 1.1 kcal/mol.

It is known that semiempirical methods underestimate the rotational barrier (or RSE) in conjugated π systems,[22b,26a] while *ab initio* methods give somewhat larger values.[22b] Thus, 2.0 kcal/mol (MINDO/3),[26b] 20.0 kcal/mol (STO-3G/4-31G),[22b,e] and 12.5 ± 1.5 (CASSCF/CASPT2N)[22e] have been reported for the benzyl radical, which has an experimental RSE value of ca. 12–13 kcal/mol.[13a,21] Our computational method (PM3-AUHF)[24,25] leads to an RSE value of 3.5 kcal/mol for the benzyl radical, which is better than earlier semiempirical estimates, but still a factor of ca. 3.6 smaller than the experimental RSE value. Nevertheless, by adjusting the RSE values of Figure 3 by this factor, a resonance stabilization of 2.9 kcal/mol for the parent cumyl radical (X = H) results. A smaller RSE for the cumyl compared to the benzyl radical was expected, since larger steric interactions in the planar conformation (0°) between the α methyl groups and the *ortho* hydrogen atoms of the phenyl group will raise its ground-state energy. These results demonstrate convincingly that electronic substituent effects on the α spin density (ρ_α) and radical stabilization energy (RSE) in the cumyl monoradicals **7** are reflected accurately by the D parameters of the *triplet diradicals* **6** and offer a new spectroscopic tool to assess electronic substituent effects in benzyl-type monoradicals.

Comparison with Other σ_{rad} Scales. The ΔD scale (Table 2) shall now be compared with the established σ_{rad} scales for benzyl-type radicals to evaluate how well it fares in reflecting electronic substituent effects of chemical systems. Only moderate correspondence is found with Arnold's EPR-derived σ_α scale ($r^2 = 0.722$, $n = 15$), which, unfortunately, does not include important substituents such as NR_2, NO_2, NH_3^+, Br, I, OH, O^-, or C≡CPh. Moreover, it should be kept in mind that Arnold's σ_α scale deals with substituted benzyl radicals and the ΔD scale

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(26) (a) Dodziuk, H. *J. Mol. Struct.* **1979**, *55*, 107. (b) Khalil, S. M.; Shansal, M. *Theor. Chim. Acta* **1977**, *46*, 23.

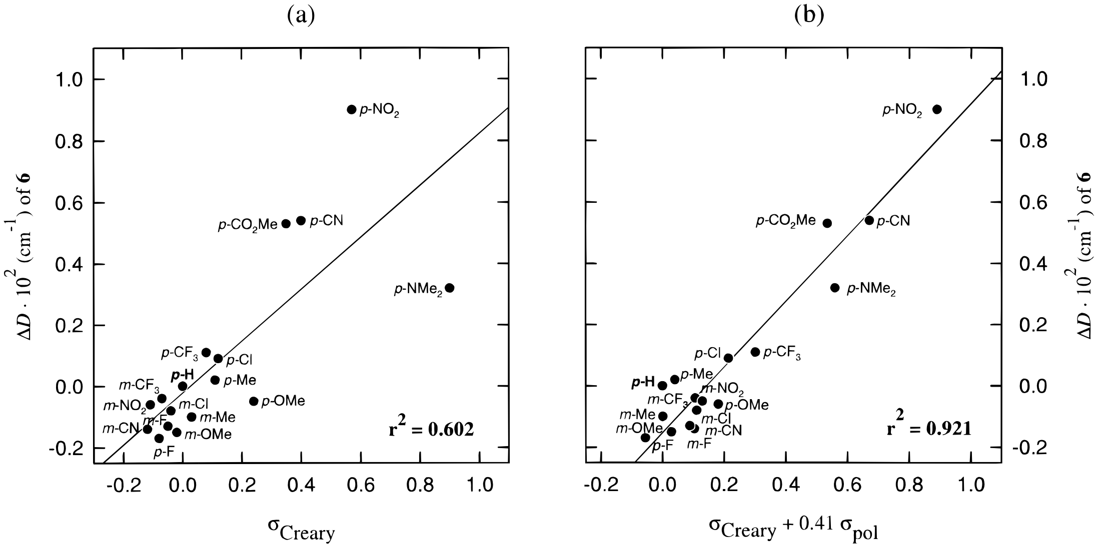

Figure 3. ΔD against the Creary σ_{rad} values for (a) direct correlation and (b) after inclusion of polar effects by a two-parameter Hammett analysis (*cf.* eq 4).

Table 2. ΔD Scale Compared with Other σ_{rad} Scales for Benzyl-Type Radicals

X	ΔD[a]	σ_α[b] ($r^2 = 0.722$)	σ_C[c] ($r^2 = 0.602$)	σ_F[d] ($r^2 = 0.929$)	σ_J[e] ($r^2 = 0.605$)	σ_D[f] ($r^2 = 0.339$)
m-C≡CPh	**−0.25**					
m-NMe$_2$[g]	**−0.23**					
m-OH	**−0.22**					
m-NH$_2$	**−0.19**					
m-O$^-$	**−0.18**					
p-F	**−0.17**	−0.011	−0.08	−0.25	0.12	−0.02
m-OMe	**−0.15**	−0.001	−0.02			0.10
m-CN	**−0.14**	−0.026	−0.12	−0.10		0.11
m-NHCOMe[g]	**−0.14**					
m-F	**−0.13**	−0.009	−0.05			0.03
m-NH$_3^+$[g]	**−0.11**					
p-OCOMe	**−0.11**	−0.005				
m-OCOMe	**−0.10**					
m-Me	**−0.09**	0.002	0.03			0.00
m-I	**−0.09**					
m-Cl	**−0.08**	−0.007	−0.04			−0.05
m-CH$_2$CH$_2$Ph[g]	**−0.07**					
m-NO$_2$	**−0.06**		−0.11	−0.04		0.01
p-OH	**−0.05**					
p-OMe	**−0.04**	0.018	0.24	−0.12	0.43	0.23
m-CF$_3$	**−0.04**	−0.017	−0.07			−0.07
H	**0.00**	**0.000**	**0.00**	**0.00**	**0.00**	**0.00**
p-Me	**0.02**	0.015	0.11	−0.02	0.39	0.15
p-O$^-$	**0.02**					
p-I	**0.04**			0.16		
p-Br	**0.05**		0.13	0.17	0.20	0.23
p-NH$_3^+$[g]	**0.08**					
p-Cl	**0.09**	0.011	0.12	0.08	0.18	0.22
p-CF$_3$	**0.11**	-0.009	0.08			−0.01
p-NHCOMe[g]	**0.22**					
p-NH$_2$[g]	**0.30**					
p-NMe$_2$[g]	**0.32**		0.90			1.00
p-CO$_2$Me	**0.52**	0.043	0.35	0.53[h]		0.33
p-CN	**0.54**	0.046	0.40	0.34		0.42
p-NO$_2$	**0.90**		0.57	0.27[i]	0.76	0.36

[a] For definition *cf.* eq 1. [b] Reference 13. [c] Reference 10. [d] Reference 9. [e] Reference 11. [f] Reference 12. [g] Hydrogenated derivatives, D value (*para*-H) 0.0506 cm^{-1}. [h] Acetyl substituent. [i] Appears too small due to steric interactions.[9b]

with the cumyl type. The distinct difference between benzyl and cumyl radicals has been elaborated by Arnold[13a] in terms of substituent effects on the zwitterionic structures of the cumyl radical. Indeed, a much better correlation ($r^2 = 0.948$) was found when the D parameters of the *triplet diradicals* were plotted *versus* the a_β hyperfine splitting constants of corresponding cumyl monoradicals.[8c]

Of the chemical σ_{rad} scales, the one with the best correspondence ($r^2 = 0.929$) is the Fisher scale (σ_F);[27] the others are definitely worse than Arnold's spectroscopic σ_α scale. The scale of particular interest for our comparison is the Creary scale (σ_C), since it provides the largest set of substituents, which spans the entire range of σ values from NMe$_2$ to NO$_2$. The direct correlation (Figure 3a) afforded only a poor correspondence ($r^2 = 0.602$, $n = 17$), in which the most serious deviations from linearity are evident for the strong electron-donating *p*-NMe$_2$ and the strong electron-accepting *p*-NO$_2$ groups.

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(27) Note that the value for the *p*-NO$_2$ substituent is not included in the correlation due to steric interactions with the *m*-CN group, *cf.* ref 9b.

Presumably, polar contributions in the transition state are at work, which encumber a reliable assessment of the electronic substituent effects in radicals. Therefore, a two-parameter Hammett analysis (eq 4) was performed,

$$\Delta D = \rho_{\mathrm{rad}}\sigma_{\mathrm{rad}} + \rho_{\mathrm{pol}}\sigma_{\mathrm{pol}} \qquad (4)$$

which substantially improved (Figure 3b) the linear correlation ($r^2 = 0.921$) when corrections for polar effects were made in terms of Hammett polar substituent constants (σ_{pol}).[28] This analysis reveals that polar effects are important in chemical σ_{rad} scales, but electronic substituent effects are predominantly radical-type in nature, as expressed by the size of the Hammett reaction constants ($\rho_{\mathrm{rad}} = 1.00$ *versus* $\rho_{\mathrm{pol}} = 0.41$).

The Δ*D* scale spans the widest range of radical substituent constants known to date, *i.e.*, from −0.25 (*m*-C≡CPh) to +0.90 (*p*-NO_2), and represents a direct probe for variations of α spin density and radical stabilization energy in cumyl radicals. For the first time the *p*-OH and *p*-NH_2 groups and their charged derivatives *p*-O^- and *p*-NH_3^+ are featured. The former, which are the simplest oxygen and nitrogen substituents, were included to evaluate the possible role of methyl substitution (*p*-OMe and *p*-NMe_2) in assisting spin delocalization. However, the Δ*D* values are very similar for *p*-OH (−0.05) *versus* *p*-OMe (−0.04) and *p*-NH_2 (+0.30) *versus* *p*-NMe_2 (+0.32), which implies analogous electronic effects on the radical and excludes any significant effect of methylation. The introduction of a strong electron-accepting group through acylation of the *O* or *N* atoms dramatically lowers the spin-accepting properties due to reduced lone-pair interaction with the radical center, as can be witnessed by the Δ*D* values for the *p*-OCOMe (−0.11) and *p*-NHCOMe (+0.22) substituents. These trends are also nicely reproduced by the semiempirical calculations of the respective α spin densities ρ_α (Figure 1). Moreover, protonation of the nitrogen lone pair results in a dramatic change in the Δ*D* value to less positive values (*p*-NH_2 = +0.30 *versus* *p*-NH_3^+ = +0.08), as would be expected from the inability of spin delocalization by conjugation for the latter. In contrast, the slightly positive Δ*D* value for the *p*-O^- (+0.02) substituent indicates a slightly higher spin-accepting nature of the negatively charged oxygen atom *versus* *p*-OH (−0.05).

Destabilizing Effect of *Meta* Substituents on Benzyl-Type Radicals. Table 2 reveals that all *meta* substituents possess negative Δ*D* values and consequently the α spin density in the corresponding cumyl monoradicals **7** is increased (Figure 1), which implies destabilization of the radical as reflected in the smaller RSE values (Figure 2). This is remarkable since *meta* substituents do not interact directly by conjugation with the radical center and should, therefore, exercise little influence. Nonetheless, such destabilizing effects have been pointed out previously by others,[9,10,13a] and several explanations have been offered. On the one hand, it was argued that for strong electron-accepting groups (*m*-CN, *m*-CF_3) the inductive withdrawal of electron density will result in increased localization of α spin density at the benzylic position either by decreasing the overlap between the interacting centers or by increasing the energy separation between the interacting orbitals.[13a] On the other hand, the participation of zwitterionic resonance structures in benzyl radicals has been proposed to be responsible.[29] Our results (Table 2 and Figure 1) show that strong electron-accepting groups (*m*-NO_2, *m*-CF_3) have only a small destabilizing influence on the cumyl radical, whereas strong electron-donating groups (*m*-OMe, *m*-NMe_2) destabilize the cumyl monoradical more efficiently. This fact suggests that the destabilizing effect on benzyl-type radicals may derive from the electron-donating propensity of the *meta* substituents. The Swain−Lupton resonance parameter *R*[28] serves well for this purpose, and a plot of the Δ*D* values of the *meta*-substituted diradicals ***m*-6** *versus* the *R* parameter (Figure 4) displays, indeed, a good linear dependence ($r^2 = 0.945$, $n = 15$). Exceptions are the *m*-CN substituent, which is in chemical σ_{rad} scales the strongest destabilizing substituent,[9,10,12,13a] while the *m*-C≡CPh substituent is the strongest in our Δ*D* scale (*cf.* Table 2). These *meta* substituents severely deviate in this correlation and have, therefore, been excluded. Interestingly, both substituents possess triple bonds, and that the latter is responsible for the deviation was demonstrated by reduction of the CC triple bond to the normal alkyl group (*m*-C≡CPh = −0.25 *versus* *m*-CH_2CH_2Ph = −0.07), which leads to a Δ*D* value in line with the linear correlation (Figure 4). These trends are also reflected by the semiempirically computed[24,25] α spin densities (*cf.* Table 1 and Figure 1). At this point it is not clear what special electronic effects operate for these triple-bonded *meta* substituents to cause such negative Δ*D* values, and for that matter, why *all* *meta* substituents, irrespective of whether they are electron donors or acceptors, localize spin at the cumyl radical site. We contend that in these cross-conjugated systems the electronic effects of the α spin center and the *meta* substituent are competing with one another in the aromatic ring such that the overall effect is spin localization at the benzylic radical site. It is in this sense that we designate the *meta* substituents as spin donors.

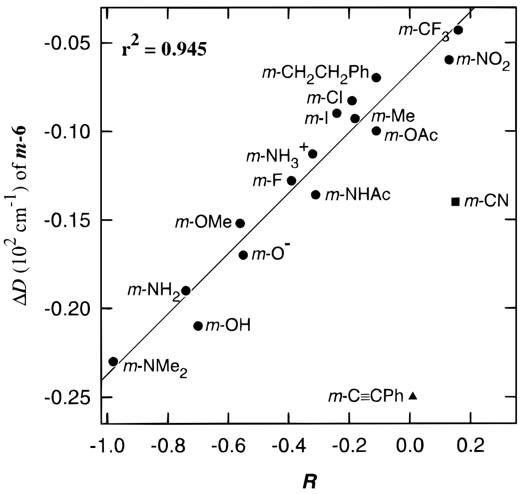

Figure 4. Δ*D* values of the *meta*-substituted *triplet diradicals* **m-6** *versus* the Swain−Lupton resonance parameter *R* (ref 28); the values for *m*-CN (■) and *m*-C≡CPh (▲) are not included in the correlation.

One may ask why these trends have not been recognized earlier since such data were available.[10,12,13a] Since the extent of the destabilizing effect in *meta*-substituted benzyl-type radicals is relatively small (*cf.* Table 2), such effects will be hidden by polar effects in the kinetic scales (e.g., *m*-CN: $\sigma_C = -0.12$ *versus* $\sigma_{\mathrm{pol}} = +0.56$), as demonstrated by the two-parameter Hammett analysis (Figure

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(28) Values taken from: Hantsch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 321.

(29) Jackson, R. A.; Moosavi, R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 885.

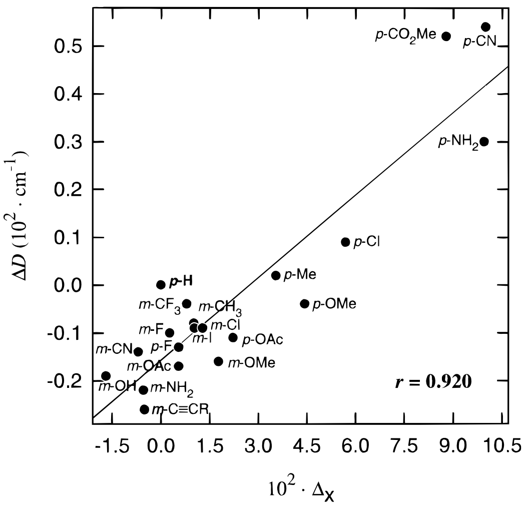
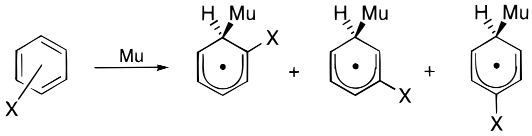


Figure 5. ΔD values of the *triplet diradicals* **6** *versus* the Δ_x parameter of substituted muonated cyclohexadienyl radicals (ref 30).

3). In the case of the spectroscopic σ_α scale, the accuracy (± 0.02 G) is diminished due to the inherent complexity of the EPR spectra for the *meta*-substituted benzyl radicals, which cover only a range of ± 0.20 G.[13] These shortcomings are not encountered in the ΔD scale, for which polar effects are nominal and the total range in the *meta* substituents covers ± 14 G with an accuracy of 1 G. We must stress that these advantages of the D parameter enable us to assess even relatively small substituent effects in unpaired electron systems.

Comparison with the Δ_x Scale for Muonated Cyclohexadienyl Radicals. Electronic substituent effects have been studied on muonated cyclohexadienyl radicals, which are formed by addition of a muon atom to substituted benzenes (eq 5).[30] From the hyperfine



(5)

coupling constants, obtained by μSR spectroscopy for a large set of *para* and *meta* substituents, the Δ_x substituent parameter was defined analogous to Arnold's σ_α scale. Since both the Δ_x and the σ_α scales correlate well,[30a,b] we were encouraged to test the correspondence between the ΔD values of the triplet diradicals **6** and the Δ_x parameter of the cyclohexadienyl radicals. Indeed, as Figure 5 reveals, a good agreement is found ($r = 0.920$) between the two ΔD and Δ_x spectral scales. For example, the *meta* substituents OH, NH_2, and C≡CR, which are not featured in any other σ_{rad} scales, exhibit in both scales substantial spin localization at the radical sites. This good correspondence between the results determined by such rather different spectroscopic tools and such structurally varied radical types as cumyl and cyclohexadienyl radicals corroborates that the present electronic substituent effects are meaningful and general to assess spin distributions in radical systems.

Conclusions

The D parameter of the *triplet diradicals* **6**, which can be regarded as a composite of two virtually independent cumyl monoradical fragments, is a sensitive experimental measure of electronic substituent effects in radicals. The excellent correlation between the D parameters of the *triplet diradicals* **6** and the calculated α spin densities of the corresponding monoradicals **7** provide strong evidence that the *triplet diradicals* **6** serve as a good model system for the reliable assessment of electronic substituent effects in benzyl-type radicals. This is further supported by the dependence of the calculated radical stabilization energies of the monoradicals **7** and the experimental D parameter. Therefore, the D parameter constitutes an alternative EPR spectroscopic scale for the evaluation of Hammett-type σ_{rad} values for even hitherto inaccessible substituents such as NH_3^+ or O^-. Comparison of the spectroscopic ΔD scale with the existing chemical σ_{rad} scales reveals that polar effects are significant in the latter, and a two-parameter Hammett treatment is necessary to provide good correspondence. Since each radical reaction is subject to its characteristic polar effects in the transition as well as ground states, we contend that spectroscopic σ_{rad} scales may provide a more reliable measure of electronic substituent effects in radicals.

Experimental Section

EPR Spectroscopy. A sample (ca. 5×10^{-4} mmol) of the azoalkanes **5** was dissolved in 0.3 mL of 2-methyltetrahydrofuran. The stock solutions were placed in an EPR sample tube and thoroughly degassed by purging with argon gas. The azoalkanes ***p*-5l** and ***m*-5l** were generated *in situ* by addition of a ca. 5-fold molar excess of dry pyridine to a sample of the azoalkanes ***p*-5p** and ***m*-5p**. The samples were sealed, and the 77 K matrix was prepared by freezing the sample in liquid nitrogen. The triplet diradicals ***p*-6g**, ***m*-6e**, and ***m*-6o** were generated directly in the cavity of a Bruker ER-420 EPR spectrometer (9.52 GHz) by UV irradiation (320−400 nm) with a 1 kW Hg/Xe high-pressure lamp at 77 K for ca. 20 min. All other triplet diradicals **6** were generated by irradiation with the 364 nm line of a INNOVA-100 CW argon ion laser (widened beam, 1.0 W MLUV, 2 min) at 77 K, and their EPR spectra were recorded with 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.[2]

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Supporting Information Available: Synthetic details and characteristic spectral data of the 1,3-propanediones **8**, 2,2-dimethyl-1,3-propanediones **9**, 4,4-dimethyl-4*H*-pyrazoles **10**, and the azoalkanes **5** and a typical EPR spectrum (***p*-6n**), a simulation of the half-field signal for the triplet diradical ***p*-6o**, and a table of the calculated spin densities of the cumyl radicals **7** (22 pages). This material is contained in libraries on microfiche, 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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