7650 *J. Org. Chem.* **2000,** *65,* 7650−7655

EPR Spectral Determination of Electronic Substituent Effects on the *D* Values of Hydrocarbon Polyradicals (Quintet and Septet Spin States) Composed of Localized 1,3-Cyclopentanediyl Spin-Carrying Units Linked by 1,3-Di- and 1,3,5-Trimethylenebenzene Ferromagnetic Couplers

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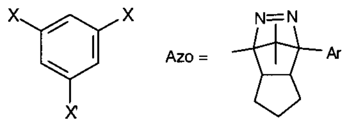
Received August 23, 2000

The parent and *p*-nitrophenyl-substituted diradicals **D-3a,b** (triplets), tetraradicals **T-3a,b** (quintets), and hexaradicals **H-3a,b** (septets) were photochemically generated in matrix-isolated form (toluene, 77 K) by successive denitrogenation of the trisazoalkanes **3a,b** and EPR spectrally characterized. In these high-spin polyradicals the spin−spin interaction within the localized spin-carrying 1,3-cyclopentanediyl diradical unit is much stronger than within the cross-conjugated ferromagnetic coupling unit. Accordingly, a change of the electronic properties in the cyclopentanediyl unit affects decisively the *D* value of the whole polyradical. Therefore, the spin-accepting *p*-nitro group reduces the *D* value of the tetra- and hexaradical in the same amount as that of the diradical. Thus, irrespective of the spin multiplicity, the substituent stabilizes electronically the triplet (**D-3a,b**), quintet (**T-3a,b**), and septet (**H-3a,b**) species with equal efficacy.

Introduction

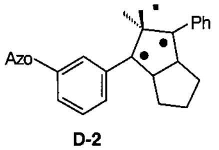
The development of organic high-spin polyradicals is of current interest in basic research as well as in materials science.[1] Compared to metal-type magnets, organic magnetic materials would open up the opportunity to combine magnetic with advantageous optical, electrical, and mechanical properties. The strategy to design organic polyradicals is to link spin-carrying fragments by ferromagnetic couplers, which induce a parallel alignment of all the spins in the molecule. Such spin alignment may be achieved by means of open-shell organic molecules. An important prerequisite for efficient ferromagnetic coupling is that the coupler and the spin carrier are not twisted out of conjugation.[2] The choice of adequate ferromagnetic couplers is quite limited. Established ones are the cross-conjugated non-Kekulé structures 1,3-di-[3] and 1,3,5-trimethylenebenzene,[4] in which the Hückel NBMOs are non-disjoint.[5] However, in the selection of an appropriate spin-carrying unit, there are numerous options, since in principle the plethora of persistent organic radicals apply.[1a]

We consider the 1,3-cyclopentanediyl diradical **D-1** to be a good spin carrier because of its triplet ground state, its remarkable persistence (several months at 77 K), and its convenient synthetic accessibility. These 1,3-cyclopentadiyl triplet diradicals, classified as localized diradicals since the two spins are not conjugated, are readily generated from the corresponding azoalkane **1**. Their electronic and structural properties may be characterized through the EPR zero-field-splitting parameters *D* and *E*, which derive from the dipole−dipole interaction between the two uncoupled spins.[6]

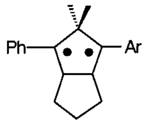


1a,b (X = H, X' = Azo)
2 (X = Azo, X' = H)
3a,b (X = X' = Azo)

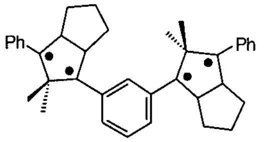
	Ar
a	Ph
b	Ar-*p*NO$_2$



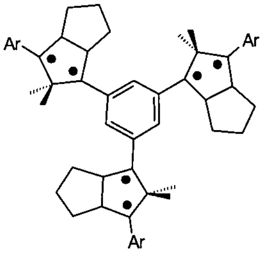
D-2



D-1a,b



T-2



H-3a,b

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[1] For reviews, see: (a) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88−94. (b) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346−351. (c) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893. (d) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 399−432. (e) Baumgarten, M.; Müllen, K. *Top. Curr. Chem.* **1994**, *169*, 1−104.

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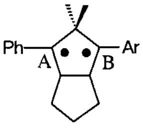
[5] (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587−4594. (b) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109−116.

10.1021/jo0012795 CCC: $19.00

The tetraradical **T-2** represents the first polyradical with a quintet-spin ground state, in which two localized 1,3-cyclopentanediyl diradicals have been linked ferromagnetically by *m*-phenylene.[7] When three 1,3-cyclopentanediyl diradical units are linked by 1,3,5-trimethylenebenzene the hexaradical **H-3** results, in which the six unpaired electron may acquire a septet spin state. Not only would the array of parallel spins be extended, but the two-dimensional structure would allow the design of dendrimeric polyradicals.[1c] Indeed, the 1,3,5-trimethylenebenzene unit has been used successfully to connect simple radicals[8] and carbenes[9] to form such high-spin polyradicals. Similarly, we have recently demonstrated that the septet hexaradical **H-3** (the first example in which localized 1,3 diradicals are ferromagnetically coupled by 1,3,5-trimethylenebenzene) possesses a septet-spin ground state.[10]

For the aryl-substituted 1,3-cyclopentanediyl triplet diradical **D-1**, we have previously shown that the *D* parameter (eq 1) is a valuable probe to assess electronic substituent effects, because the *D* value is a linear function of the spin density at the α position of the cumyl-radical fragment.[6] Thus, the higher the spin-accepting propensity of the aryl substituent, the more effectively delocalized is the unpaired electron into the aromatic ring and, consequently, the lower the spin density at the cumyl-radical site as manifested by the lower *D* value. Such electronic substituent effects have only been examined so far in high-spin ($S > 1$) polycarbenes.[11] Accordingly, the incentive of the present work was to explore the change of the spin density caused by substituents on the aryl ring of the 1,3-cyclopentanediyl spin carrier in the high-spin ($S > 1$) polyradicals **T** and **H**. For this purpose, the unsubstituted trisazoalkane **3a** and the *p*-nitro-substituted trisazoalkane **3b** were synthesized and photodenitrogenated to the corresponding tetraradicals **T-3a** and **T-3b** as well as hexaradicals **H-3a** and **H-3b**, and their *D* values were determined by EPR spectroscopy under matrix isolation at 77 K. Herein we present the results of this investigation.



D-1

$$D_{\mathbf{D\text{-}1}} = \frac{3\,\mu_0\, g^2\, \mu_B}{16\,\pi} \cdot \frac{\rho_A\ \rho_B}{d_{AB}^{\,3}} \qquad (1)$$

ρ_A, ρ_B ≡ spin densities of the monoradical fragments

Results

Synthesis. The precursor for the hexaradicals **H-3a** and **H-3b**, namely the trisazoalkanes **3a** and **3b**, were prepared in a seven-step sequence, in which the key step entailed amine-catalyzed trimerization[12] of the acetylene functionality of the dione **6**[13] to generate the central benzene ring of the hexaketone **7** (Scheme 1). After generation of the trisisopyrazole **8** by reaction of the hexaketone **7** with hydrazine hydrate (90% yield for **8a** and 95% for **8b**), the photolabile trisazoalkanes **9** were obtained by 3-fold cycloaddition with cyclopentadiene (60% yield for **9a** and 71% for **9b**). In the case of the nitro derivative **9b**, instead of the Pd-catalyzed hydrogenation used for the unsubstituted case **9a** (95% yield) which also reduces the nitro group, the double bond was saturated with diimide[14] (44% yield). On photolysis, the trisazoalkane **9a** gave cleanly the trishousane **10a** (94% yield) as a mixture of diastereomers. In analogy to the synthesis of the *p*-nitro-substituted monohousane,[15] the trishousane **10b** was obtained by thermolysis. The moderate yield of 40% is due to the formation of undesirable side products during the long reaction time. The bisazoalkane **2** was synthesized as described earlier.[7]

EPR Spectral Data. Toluene solutions (ca. 8 μM) of the particular trisazoalkane were frozen at 77 K, and photochemical extrusion of dinitrogen was effected by irradiation with the 333-nm line of the argon-ion laser.[16] Short-time photolysis (ca. 3 min) of the trisazoalkanes **3a** produced an EPR spectrum, which was virtually superimposable to that of the irradiated bisazoalkane **2** (Figure 1). Since the irradiated bisazoalkane **2** gave a mixture of the triplet diradical **D-2** and quintet tetraradical **T-2** (Figure 1a),[7] we anticipated that on short irradiation of the trisazoalkane **3a** also a mixture of the diradical **D-3a** and tetraradical **T-3a** would be formed. Indeed, the EPR spectrum measured for the trisazoalkane **3b** after 3-min irradiation was similar to that observed for the bisazoalkane **2**, with the only difference that the EPR lines of the irradiated **3b** are closer spaced (Figure 1c). This EPR spectrum was assigned to the diradical **D-3b** and tetraradical **T-3b**, whose *D* values are significantly smaller than those for the corresponding polyradicals **D-3a** and **T-3a** (Table 1, entries 2 and 3).[17]

On further irradiation of the trisazoalkane **3a**, new signals appeared which intensified, while the **T-3a** signals stopped growth (Figure 2a). The peaks marked with H in the time profile are attributed to the hexaradical **H-3**, which is formed from the tetraradical **T-3a** by photodenitrogenation. Since prolonged irradiation did not change the ratio of the signal intensities for the diradical, tetraradical, and hexaradical, the *D* and *E* value of the hexaradical **H-3a** had to be extrapolated from the composite spectrum. For this purpose, computer simulation

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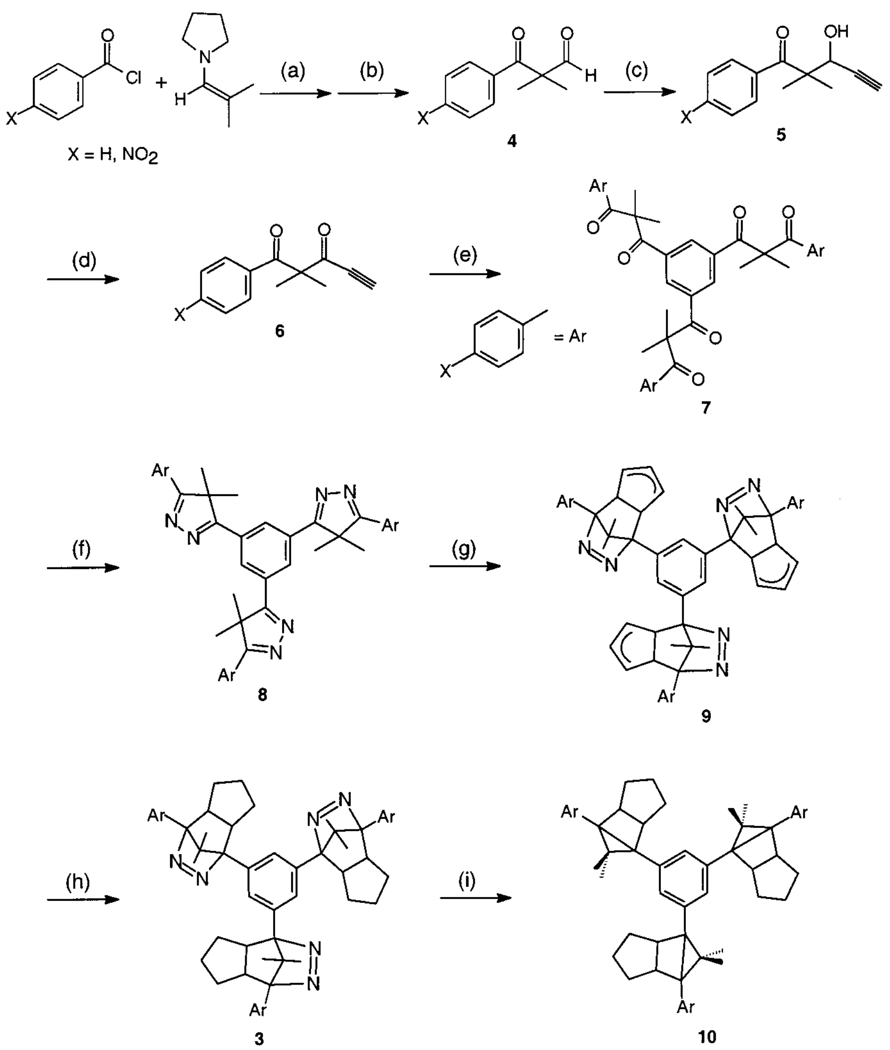
(16) A detailed study of the photochemistry on the trisazoalkane by UV and EPR spectroscopy has been submitted for publication in *J. Org. Chem.*

(17) The *D* values of the tetraradicals **T-3a** and **T-3b** were determined from the outermost characteristic quintet EPR signals, which are separated by 6*D*.

Scheme 1. Synthesis of the Trisazoalkanes 3a and 3b[a]



[a] Reagents and conditions: (a) Et_2O, ca. 20 °C, 16 h; (b) HCl, Et_2O, ca. 20 °C, 4 h; (c) C_2H_5BrMg, HC≡CH, THF; X = H: 0 °C → ca. 20 °C, 18 h; X = NO_2: −60 °C, 6 h; (d) X = H: CrO_3, H_2SO_4, acetone, 0 °C → ca. 20 °C, 7 h; X = NO_2: Dess−Martin periodinane,[13] CH_2Cl_2, ca. 20 °C, 2 h; (e) $HNEt_2$ (0.13 equiv.), *o*-xylol, reflux, 3 d; (f) $N_2H_4 \times H_2O$ (5 equiv), $CHCl_3$; X=H: reflux, 16 h; X = NO_2: ca. 20 °C, 2 d; (g) CF_3COOH (1.5 equiv), cyclopentadiene, CH_2Cl_2, 0−5 °C, 3 d; (h) X = H: Pd/C, H_2, benzene, ca. 20 °C, 24 h; X = NO_2: $N_2H_4{\cdot}H_2O$ (12 equiv), $PhI(OAc)_2$ (5 equiv), $NaHCO_3$, CH_2Cl_2, ca. 20 °C, 3 h; (i) X = H: (λ = 333−364 nm, 1.3 W, ca. 10 min, benzene; X = NO_2: 80 °C, d_6-benzene, $NaHCO_3$, 5 d.

and spectral subtraction was conducted; the best fit between the experimental and simulated spectrum was achieved for $D_{\mathbf{H-3a}} = 0.0091$ cm^{-1} and $E_{\mathbf{H-3a}} = 0.0002$ cm^{-1}.[10] (The *D* and *E* parameters for the particular polyradical have been coded by subscripts of the respective structure numbers).

In analogy to the unsubstituted trisazoalkanes **3a**, on further irradiation of the nitro derivative **3b**, new signals also appeared. These occur at almost the same positions as the EPR signals for the **H-3a** species and were, consequently, assigned to the hexaradical **H-3b**. Since the symmetry of both hexaradicals **H-3a** and **H-3b** is the same, the *E* value (0.0002 cm^{-1}) of the unsubstituted hexaradical **H-3a** was adopted for the nitro-substituted **H-3b**; this considerably simplifies the simulation of the EPR spectrum for the hexaradical **H-3b**. In this manner, for the nitro-substituted hexaradical **H-3b** the *D* parameter was found to have the value $D_{\mathbf{H-3b}} = 0.0082$ cm^{-1} (Figure 2c), which is appreciably lower than for the unsubstituted **H-3a** case (see Table 1, entry 4).

The multitude of peaks in the simulated spectrum (Figure 2c) arises for the following reasons: In a polycrystalline matrix of an axial-symmetric spin system ($E \approx 0$), there are only two orientations of the molecular axes with respect to the external magnetic field, which absorb at distinct magnetic field strength.[18] In the case of a septet-spin system with axial symmetry, six $\Delta m_s = \pm 1$ magnetic dipole transitions occur for each of the two orientations, such that 12 peaks are expected in the EPR spectrum for a septet-spin polyradical. Each of the six positive EPR signals has a negative counterpart, and the separations of corresponding pairs of positive and negative peaks are given by *1D*, *2D*, *3D*, *5D*, *6D*, and *10D*, which are the eigen-energies of the septet spin-state Hamiltonian.

In view of the relatively high amount of the nitro-substituted tetraradical **T-3b** in the EPR spectrum of the irradiated trisazoalkane **3b**, the *3D* signals of the hexaradical **H-3b** are less pronounced in the EPR spectrum (Figure 2b) of the irradiated trisazoalkane **3b** compared to **H-3a** from **3a** (Figure 2a), for which the *3D* signals

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(18) Kirmse, R.; Stach, J. *ESR Spektroskopie − Anwendungen in der Chemie*; Akademie Verlag: Berlin, 1985; pp 39−61.

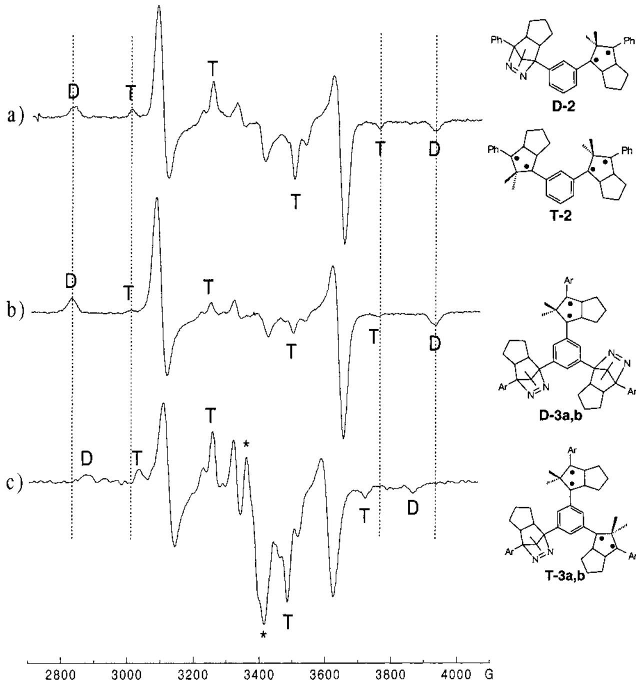


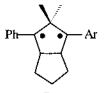
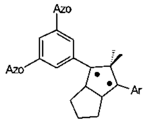
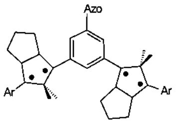
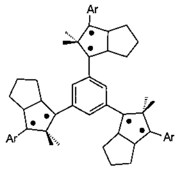
Figure 1. (a) EPR spectrum of the bisazoalkane **2** in toluene matrix, assigned to a mixture of the triplet diradical **D-2** and the quintet tetraradical **T-2**. (b) EPR spectrum of the trisazoalkane **3a** in toluene matrix, assigned to a mixture of the triplet diradical **D-3a** and the quintet tetraradical **T-3a**. (c) EPR spectrum of the trisazoalkane **3b** in toluene matrix, assigned to a mixture of the triplet diradical **D-3b** and the quintet tetraradical **T-3b** (doublet impurities are labeled with an asterix); characteristic signals of the diradical and tetraradical are labeled with D and T.

are about as intensive as the neighboring tetraradical signals T (compare Figures 2b and 2a). This makes an unequivocal assignment of the nitro-substituted hexaradical **H-3b** more difficult; however, fortunately the outermost *10D* signals are more pronounced and unambiguously pertain to the hexaradical **H-3b**.

Persistence. The polyradical mixtures obtained from the irradiated trisazoalkanes **3a** and **3b** stand out for their remarkable persistence. For example, the nitro-substituted polyradical mixture was stored for five months at 77 K, and no significant decay of the triplet, quintet, or septet EPR signals was observed! Since the signals of the polyradical mixture from the trisazoalkane **3a** still persist at 120 K in a MTHF as well as toluene matrix,[19] these polyradicals are less persistent than the polybrominated 1,3,5-tris{2-[4-(phenylcarbeno)phenyl]-ethynyl}benzene[20] (survives even at 140 K in MTHF matrix), but more so than the structurally related 1,3,5-tris(phenylmethylene)benzene.[9a] The latter triscarbene decomposes in rigid glasses already at 85 K.[20,21]

The Nitro Chromophore for Polyradical Generation. Irradiation of the nitro-substituted azoalkane **1b** generated the triplet diradical **D-1b**, which expectedly cyclized on warm-up to the corresponding housane (Scheme 2).[15] When an independently synthesized nitro-substituted housane sample was irradiated, apart from monoradical (doublets) impurities, the characteristic EPR signals for the triplet diradical **D-1b** were also observed. Unquestionably, the nitroaryl group served as chromophore for the photochemical bond fission in the housane; presumably, the strained σ bond is hyperconjugated with the π system of the aryl ring, which facilitates fragmentation.[22] When this photoactivity of the nitroaryl chromophore, a potentially attractive photochemical access to polyradicals, was attempted to be employed for the generation of the hexaradical **H-3b** from the nitro-substituted trishousane **10b**, irradiation with the 351-nm line of the argon-ion laser (0.64 W) afforded only the triplet diradical **D-10b**; the tetraradical **T-10b** or hexaradical **H-3b** was not observed even under a variety of irradiating conditions. Warm-up of the matrix sample revealed an intractable complex product mixture (mainly unreacted trishousane **10b**) upon ^{1}H NMR spectral analysis, and further efforts along these lines were abandoned.

Table 1. Experimental Zero-Field Parameters *D* and *E* of Substituted Di-, Tetra-, and Hexaradicals

entry	polyradicals[a]	*D/hc* [b] (*E/hc*) [cm^{-1}] Ar = C_6H_5 (**a**)	 Ar = C_6H_4-NO_2-*p* (**b**)	relative *D* value[c]
1	 **D-1**	0.0507 (0.0005)[d]	0.0455 (0.0005)[d]	0.90
2	 **D-3**	0.0508 (0.0005)	0.0463 (0.0005)	0.91
3	 **T-3**	0.0116 (0.0022)	0.0107 (0.0022)	0.92
4	 **H-3**	0.0091 (0.0002)	0.0082 (0.0002)	0.90

[a] Generated by photolysis of the corresponding azoalkane in a toluene matrix at 77 K. [b] *D*/hc values of the polyradicals, estimated error ± 0.0001 cm^{-1}. [c] *D* value of *p*-nitro-substituted polyradical divided by the one of the unsubstituted polyradical. [d] Reference 7.

Discussion

The comparison of the absolute *D* values of the di-, tetra-, and hexaradicals **D-1**, **D-3**, **T-3**, and **H-3** (Table 1) reveals that $D_{\mathbf{T-3}}$ value of the tetraradical **T-3** is much smaller than $D_{\mathbf{D-3}}$ value of the corresponding diradical **D-3** (entries 2 and 3). In contrast, the difference between the $D_{\mathbf{T-3}}$ and $D_{\mathbf{H-3}}$ values of the respective tetra- and hexaradicals is marginal (entries 3 and 4). The reduction of the $D_{\mathbf{T-3}}$ compared to the $D_{\mathbf{D-3}}$ values was expected since it was already experimentally observed for other

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(19) No significant change of the *D* value was detected when the sample was measured in the temperature range between 4 and 120 K.

(20) Tomioka, H.; Hattori, M.; Hirai, K.; Sato, K.; Shiomi, D.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1998**, *120*, 1106−1107.

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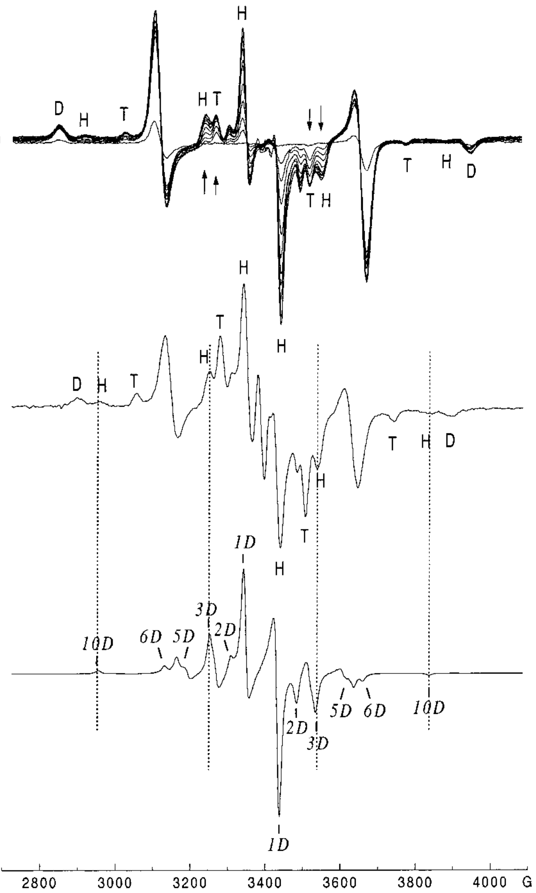


Figure 2. (a) Superimposed EPR spectra for the irradiation of the trisazoalkane **3a** in toluene matrix as a function of time; characteristic signals of the diradical **D-3**, the tetraradical **T-3**, and the hexaradical **H-3** are labeled by D, T, and H. (b) EPR spectrum for the irradiation of the trisazoalkane **3b** in toluene matrix. (c) Simulation of the septet spin state for hexaradical **H-3b** with $D_{\mathbf{H-3b}} = 0.0082$ cm^{-1} and $E_{\mathbf{H-3b}} = 0.0002$ cm^{-1}.

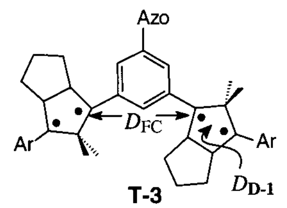
m-phenylene-coupled spin-carrying units (carbenes,[23] cyclobutanediyl,[24] and trimethylenemethane[25] diradicals) and also supported by theoretical considerations.[23] Thus, to assess the *D* parameter for such polyradical species, Itoh proposed the simple additive relation in eq 2 for the Hamiltonian *H* of quintet-spin systems,[23] made up of two

$$H = H^{SC}_{(1)} + H^{SC}_{(2)} + H^{FC}_{(1,2)} \qquad (2)$$

$H^{SC}_{(1)}, H^{SC}_{(2)}$ ≡ spin hamiltonians for the spin-carrying units 1 and 2

$H^{FC}_{(1,2)}$ ≡ spin hamiltonian for the ferromagnetic coupler between the spin carriers 1 and 2

spin-carrying units (SC) that weakly interact through a ferromagnetic coupler (FC). Application of this formula leads to eq 3 for the tetraradical **T-3**, which consists of two structurally identical cyclopentanediyl diradical units



$$D_{\mathbf{T\text{-}3}} = \frac{D_{\mathbf{D\text{-}1}} + D_{FC}}{3} \qquad (3)$$

$D_{FC} \equiv D$ parameter of the ferromagnetic coupler

with the same zero-field splitting tensor $D_{\mathbf{D-1}}$ and a *m*-phenylene-type coupling unit with D_{FC}. For necessity and convenience we assume that the D_{FC} value is about the same as that for *m*-phenylene, i.e., $D_{m\text{-phenylene}} = 0.0110$ cm^{-1}.[26] Since the latter is much smaller than the $D_{\mathbf{D-1}}$ value (0.0507 cm^{-1}) of the diradical **D-1**, the D_{FC} term may be neglected in eq 3, and consequently the $D_{\mathbf{T-3}}$ value of the tetraradical **T-3** should be about one-third of the $D_{\mathbf{D-1}}$ value for the diradical **D-1**. The experimental data in Table 1 (entries 1 and 3) for the *D* parameter substantiate this expected trend at least qualitatively. Evidently, the weak spin–spin interaction in the cross-conjugated *m*-phenylene diradical, as reflected by the small $D_{m\text{-phenylene}}$ value, is responsible for the much lower *D* value of the tetraradical **T-3** compared to the diradical **D-1** as well as **D-3**.

That the observed $D_{\mathbf{H-3}}$ parameter of the hexaradical **H-3a** is a bit smaller than that for the tetraradical **T-2** and **T-3a** (Table 1, entries 3 and 4) is in accord with theoretical and experimental results for related di- and triradical pairs (Table 2). In fact, on the basis of theoretical considerations, it was concluded that the ratio of the *D* values for structurally related di- and triradical pairs should be constant.[8a,27] This constancy was confirmed for a set of 1,3,5-trimethylenebenzene-coupled triradicals[8a] and *m*-phenylene-coupled diradicals,[28] for which ratios of 0.69 and 0.71 were obtained (Table 2). For the pair of the structurally akin tetraradical **T-3** (contains the *m*-phenylene-coupled diradical species) and the hexaradical **H-3** (contains the 1,3,5-trimethylenebenzene-coupled triradical species), the $D_{\mathbf{H-3}}/D_{\mathbf{T-3}}$ ratio is 0.78 (Table 2). This is in excellent agreement with the ratios of above-mentioned di- and triradicals and corroborates our EPR-spectral assignment.

The experimental data in Table 2 reveal that the absolute *D* values of the polyradical **T-3** and **H-3** are larger compared to those corresponding triphenylmethyl-type di- and triradicals in Table 2. This is due to the higher spin density at the radical sites of the cyclopentanediyl-type versus the triphenylmethylene-type spin carriers. In the latter, the spin is more effectively delocalized over the three adjacent phenyl rings and, expectedly, the *D* value should be lower since the *D* parameter depends linearly on the spin density (eq 1).[6]

The interdependence between the experimental *D* parameter and the theoretical spin density in eq 1 permits assess to electronic substituent effects in high-

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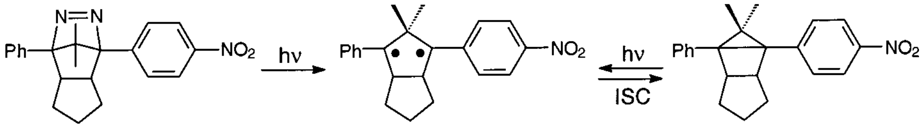
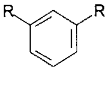
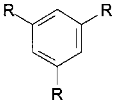
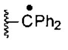
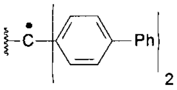
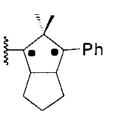
Scheme 2. Generation of the Nitro-Substituted Triplet Diradical D-1b Either by Irradiation of the Azoalkane or the Housane with the 351- or 364-nm Line of an Argon-Ion Laser



1b **D-1b**

Table 2. Ratio of *D* Values for Structurally Related Polyradicals

polyradicals	D/hc [cm^{-1}]		ratio of D values[a]
R$_{\text{substituent}}$			
	0.0069[b]	0.0049[b]	0.71
	0.0062[c]	0.0043[c]	0.69
	0.0116	0.00907	0.78

[a] *D* value of the 1,3,5-trimethylenebenzene polyradical divided by that of the *meta*-phenylene polyradical. [b] Ref 24. [c] Ref 8a.

spin species through EPR-spectral measurements, as we have amply demonstrated for the triplet diradicals **D-1** with the localized 1,3-cyclopentanediyl spin carriers.[6] Similar substituent effects have been probed here; the results for the *p*-nitro group are given in Table 1. Unfortunately, the synthetic chore to prepare additional aryl-substituted derivatives turned out to be too difficult through the acetylation–trimerization route (Scheme 1) to generate the required hexaketone starting materials. Nevertheless, the *p*-nitro substituent is one of the strongest radical-stabilizing spin acceptors[29] to provide the answer to our quest.

The results in Table 1 show that the *D* values of *p*-nitro-substituted di-, tetra-, and hexaradicals **D-1b**, **D-3b**, **T-3b**, and **H-3b** are significantly smaller than those of the corresponding unsubstituted polyradicals **D-1a**, **D-3a**, **T-3a**, and **H-3a**. Conspicuously, the relative *D* values (Table 1, fifth column) for all the listed high-spin systems are ca. 0.9. This influence of the *p*-nitro group on the *D* parameter has already been reported[15] for the simplest representative of high-spin polyradicals, namely the 1,3-cyclopentanediyl triplet diradical pair **D-1a**,**b**, which has been explained in terms of the better delocalization by the spin-accepting *p*-nitro substituent. Consequently, compared to the unsubstituted diradicals **D-1a** and **D-3a**, the *p*-nitro group in the diradicals **D-1b** and **D-3b** diminishes the spin density of the benzyl position and therewith the *D* value of the diradical is correspondingly reduced (Table 1, entries 1 and 2).

To interpret the *p*-nitro substituent effect on the *D* value of the tetraradicals **T-2** and **T-3**, eq 3 must again be considered. Since the *p*-nitro substituent is placed on the outer phenyl rings of the spin-carrying units, the ferromagnetic coupler is the same for the tetraradicals **T-3a** and **T-3b**. As already mentioned, the D_{FC} value of *m*-phenylene is much smaller than $D_{\mathbf{D-1a}}$ and also $D_{\mathbf{D-1b}}$ and therewith negligible in eq 3. Consequently, the $D_{\mathbf{T-3}}$ value of the tetraradical **T-3** is mainly determined by the $D_{\mathbf{D-1}}$ value of the **D-1** diradical unit. The $D_{\mathbf{T-3b}}/D_{\mathbf{T-3a}}$ ratio of the *p*-nitro-substituted (**T-3b**) and unsubstituted (**T-3a**) tetraradicals should be the same as the $D_{\mathbf{D-1b}}/D_{\mathbf{D-1a}}$ ratio of the corresponding **D-1b** and **D-1a** diradicals. Indeed, the data in Table 1 confirm this expectation, since the ratios are 0.90 and 0.92 (Table 1, entries 1 and 3). From eq 1 it is evident that the $D_{\mathbf{D-1b}}/D_{\mathbf{D-1a}}$ ratio is equal to the ratio of the corresponding spin densities, and indeed the semiempirically (PM3) calculated value of 0.908[30] is in excellent accord with the experimental ratio of 0.90 (Table 1, entry 1) obtained from the respective *D* values.

For the hexaradicals **H-3a,b**, the $D_{\mathbf{H-3b}}/D_{\mathbf{H-3a}}$ ratio is the same value as the $D_{\mathbf{T-3b}}/D_{\mathbf{T-3a}}$ and $D_{\mathbf{D-3b}}/D_{\mathbf{D-3a}}$ ratios for the corresponding tetraradicals **T-3a,b** and diradicals **D-3a,b** (Table 1, entries 3 and 4). Therefore, the spin-accepting *p*-nitro group exercises the same electronic influence on the *D* value of the hexaradical as on the corresponding tetraradicals and diradicals. This correspondence is expected from eq 3 because the *D* value of the tetraradical **T-3** and hexaradical **H-3** is dominated by the spin-carrying cyclopentanediyl unit and the influence of the weakly interacting 1,3-dimethylene- and 1,3,5-trimethylenebenzene ferromagnetic couplers is negligible.

In summary, it has been demonstrated that the *D* parameter of the tetraradicals **T-3a,b** and hexaradicals **H-3a,b** is mainly determined by the spin density of the localized 1,3-cyclopentanediyl spin carrier. Thus, the contribution by the 1,3-dimethylene- as well as 1,3,5 trimethylenebenzene ferromagnetic coupler is essentially negligible. Accordingly, the efficacy of spin delocalization by the spin-accepting *p*-nitro group is about the same for the herein examined polyradicals with triplet-, quintet-, and septet-spin ground states.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung and the Fonds der Chemischen Industrie.

Supporting Information Available: Synthesis and photochemistry of the trisazoalkanes **3a,b**, and the EPR spectroscopy of the polyradicals **T-3a,b** and **H-3a,b**. This material is available free of charge in the Internet at http://pubs.acs.org.

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