

About monoradicals, triplet diradicals and higher spin states: Understanding electronic substituent effects through EPR and time-resolved UV spectroscopy

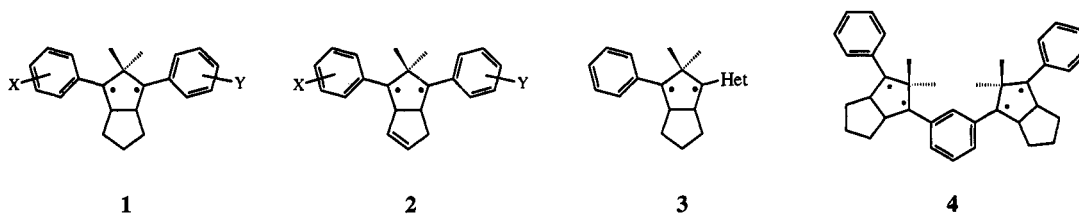
Waldemar Adam^{*a}, Claus van Barneveld^a, Oliver Emmert^a, Heinrich M. Harrer^a, Fumio Kita^a, A. Sampath Kumar^a, Wiebke Maas^a, Werner M. Nau^b, Santhapuram H. K. Reddy^a and Jakob Wirz^b

Institute of Organic Chemistry^a, University of Würzburg, Am Hubland, D-97074 Würzburg, FRG
Institute of Physical Chemistry^b, University of Basel, Klingelbergstr. 80, CH-4056 Basel, Switzerland

Abstract: Electronic substituent effects on the α spin density (ρ_α) and radical stabilization (RSE) of benzyl-type monoradicals are reflected accurately by the D parameters of the triplet diradicals **1** and **2**. Hence, the present EPR-spectroscopic ΔD scale offers a novel mechanistic tool to assess radical properties. This concept has been extended to heteroaromatic π systems, *i.e.* pyridines, furanes and thiophenes, which show the general applicability of the model presented herein. Also the ISC rates of the triplet 1,3-cyclopentanediyls **1** and **2** depend on the type of aryl substitution. Whereas the D parameter of the localized triplet diradicals are determined by the spin densities at the radical sites and the distance of separation between the spin centers, the ISC rates are dictated by the balance of *through-space* and *through-bond* interactions, which are a function of the electronic properties of the NBMO's in the two-electron-two-orbital model. When two localized 1,3-cyclopentanediyli spin-bearing units are attached to *meta*-phenylene as ferromagnetic coupler, the novel quintet tetraradical **4** results, which not only displays interesting paramagnetic behavior, but also unexpected optical properties.

INTRODUCTION

Cyclopentane-1,3-diyl triplet diradicals, classified as localized diradicals, may be readily generated from the corresponding 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) precursors by photo-deazetation [1]. Two spectroscopic methods are available for the investigation of such species, on the one hand matrix EPR spectroscopy, which affords the zero-field splitting (ZFS) parameter D [2], and on the other hand time-resolved transient spectroscopy in solution, which yields the intersystem crossing rates (ISC) for the triplet ground state [3]. The former is a measure for the dipole-dipole interaction in such localized diradicals, whereas the latter determines the influence which governs the spin-orbit coupling (SOC). Both spectroscopic methods require sufficiently persistent species for optimal results, which may be accomplished by aryl substitution of the radical sites. The persistence of such diradicals in glass matrices may be enhanced from seconds up to several hours even at 77 K for EPR spectroscopy [3] and allows an accurate determination of the decay kinetics on the μ s time scale by time-resolved UV spectroscopy. In the present work we have focused our attention on the mono- and disubstituted cyclopentane-1,3-diyl triplet diradicals **1** and **2** (symmetrically disubstituted), which have served as „work-horses“ to



investigate electronic substituent effects on the EPR D parameter [4] and on the ISC rates of such species [3]. Derivatives **3** allowed us to probe conjugating effects by heteroaromatic π systems and the higher spin species **4** represents the first long-lived quintet tetraradical of this type.

TABLE 1: *D* Parameters, ΔD Values and ISC Rate Constants of the Triplet Diradicals **1** and **2**

X	Y	$ D/hcl $ ^{a)}	ΔD ^{b)}	k_{ISC} ^{c)}	X	Y	$ D/hcl $ ^{a)}	ΔD ^{b)}	k_{ISC} ^{c)}		
1	<i>p</i> -NO ₂	<i>p</i> -NO ₂	0.0416	+0.90	0.88 ± 0.051	1	<i>p</i> -OMe	<i>p</i> -H	0.0509	-0.03	5.1 ± 0.1
2	<i>p</i> -NO ₂	<i>p</i> -NO ₂	0.0414	+0.90	1.6 ± 0.1	1	<i>p</i> -OMe	<i>p</i> -OMe	0.0510	-0.04	7.0 ± 0.1
1	<i>p</i> -CN	<i>p</i> -CN	0.0448	+0.58	1.05 ± 0.02	2	<i>m</i> -CF ₃	<i>m</i> -CF ₃	0.0508	-0.04	3.6 ± 0.6
2	<i>p</i> -CN	<i>p</i> -CN	0.0449	+0.55	1.8 ± 0.1	2	<i>p</i> -OMe	<i>p</i> -OMe	0.0509	-0.05	15.0 ± 0.2
2	<i>p</i> -CO ₂ Me	<i>p</i> -CO ₂ Me	0.0451	+0.53	—	2	<i>p</i> -OH	<i>p</i> -OH	0.0509	-0.05	15.7 ± 0.9 ^{f)}
1	<i>p</i> -NO ₂	<i>p</i> -H	0.0454	+0.52	1.7 ± 0.1	2	<i>m</i> -NO ₂	<i>m</i> -NO ₂	0.0510	-0.06	—
1	<i>p</i> -NMe ₂	<i>p</i> -NMe ₂	0.0474	+0.32	—	1	<i>m</i> -EtPh	<i>m</i> -EtPh	0.0511	-0.07	—
1	<i>p</i> -NH ₂	<i>p</i> -NH ₂	0.0476	+0.30	7.6 ± 0.1	2	<i>m</i> -Cl	<i>m</i> -Cl	0.0512	-0.08	3.9 ± 0.2
1	<i>p</i> -CN	<i>p</i> -H	0.0477	+0.29	1.88 ± 0.02	2	<i>m</i> -I	<i>m</i> -I	0.0513	-0.09	6.9 ± 0.1
1	<i>p</i> -SEt	<i>p</i> -SEt	0.0477	+0.29	—	2	<i>m</i> -Me	<i>m</i> -Me	0.0513	-0.09	6.2 ± 0.6
1	<i>p</i> -CO ₂ Me	<i>p</i> -H	0.0479	+0.27	2.01 ± 0.02	2	<i>m</i> -OAc	<i>m</i> -OAc	0.0514	-0.10	4.1 ± 0.3
1	<i>p</i> -SO ₂ Et	<i>p</i> -SO ₂ Et	0.0480	+0.26	—	2	<i>p</i> -OAc	<i>p</i> -OAc	0.0515	-0.11	7.0 ± 0.3
1	<i>p</i> -NHAc	<i>p</i> -NHAc	0.0484	+0.22	—	1	<i>m</i> -NH ₃ ⁺	<i>m</i> -NH ₃ ⁺	0.0517	-0.11	—
1	<i>p</i> -POPh ₂	<i>p</i> -POPh ₂	0.0487	+0.19	—	2	<i>m</i> -F	<i>m</i> -F	0.0517	-0.13	—
1	<i>p</i> -SOEt	<i>p</i> -SOEt	0.0490	+0.16	—	1	<i>m</i> -NHAc	<i>m</i> -NHAc	0.0520	-0.14	—
1	<i>p</i> -NH ₂	<i>p</i> -H	0.0493	+0.13	6.2 ± 0.2	2	<i>m</i> -CN	<i>m</i> -CN	0.0518	-0.14	3.3 ± 0.1
2	<i>p</i> -CF ₃	<i>p</i> -CF ₃	0.0493	+0.11	2.8 ± 0.1	2	<i>m</i> -OMe	<i>m</i> -OMe	0.0519	-0.16	5.8 ± 0.7
1	<i>p</i> -Cl	<i>p</i> -H	0.0502	+0.04	3.3 ± 0.1	2	<i>p</i> -F	<i>p</i> -F	0.0521	-0.17	8.2 ± 0.3
2	<i>p</i> -Cl	<i>p</i> -Cl	0.0495	+0.09	5.9 ± 0.1	2	<i>m</i> -O ⁻	<i>m</i> -O ⁻	0.0522	-0.18	—
1	<i>p</i> -NH ₃ ⁺	<i>p</i> -NH ₃ ⁺	0.0496	+0.08	—	2	<i>m</i> -NH ₂	<i>m</i> -NH ₂	0.0523	-0.19	—
2	<i>p</i> -Br	<i>p</i> -Br	0.0499	+0.05	10.4 ± 0.1	2	3,5-Me	3,5-Me	0.0524	-0.20	—
2	<i>p</i> -I	<i>p</i> -I	0.0500	+0.04	17.5 ± 0.3	2	<i>m</i> -OH	<i>m</i> -OH	0.0526	-0.22	6.0 ± 0.8 ^{f)}
2	<i>p</i> -O ⁻	<i>p</i> -O ⁻	0.0502	+0.02	—	1	<i>m</i> -NMe ₂	<i>m</i> -NMe ₂	0.0528	-0.22	—
2	<i>p</i> -Me	<i>p</i> -Me	0.0502	+0.02	8.7 ± 0.2	2	3,5-OAc	3,5-OAc	0.0527	-0.23	—
1	<i>p</i> -Me	<i>p</i> -H	0.0505	+0.01	3.9 ± 0.1	2	<i>m</i> -C≡CPh	<i>m</i> -C≡CPh	0.0529	-0.26	—
1	<i>p</i> -H	<i>p</i> -H	0.0506	0.00 ^{d)}	3.7 ± 0.1	2	3,5-OMe	3,5-OMe	0.0537	-0.33	—
2	<i>p</i> -H	<i>p</i> -H	0.0504	0.00 ^{e)}	5.9 ± 0.2	2	3,5-OH	3,5-OH	0.0547	-0.43	—

a) Measured in a MTHF glass matrix at 77 K, values given in cm^{-1} , error $\pm 0.0001 \text{ cm}^{-1}$; b) $\Delta D = D_H - D_X$, values given in 10^2 cm^{-1} , arranged in descending order from most positive (best spin acceptor) to most negative (best spin donor) ΔD values; c) triplet diradicals were generated from the corresponding azoalkanes by flash photolysis with a XeF excimer laser (351 nm) in degassed benzene solutions at 20.0 °C, values given in 10^5 s^{-1} ; d) parent system for the diradicals **1**; e) parent system for the diradicals **2**; f) measured in degassed acetonitrile at 20.0 °C.

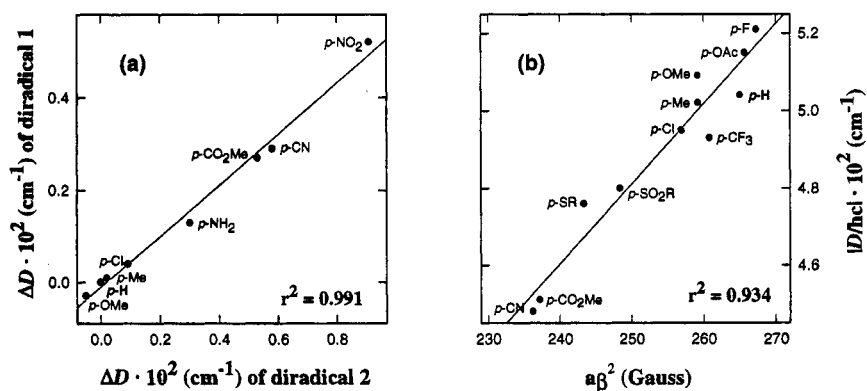


Figure 1: *D* values (a) of the monosubstituted **1** versus symmetrically disubstituted triplet diradicals **2** and (b) of the symmetrically disubstituted diradicals **2** versus a_β^2 hyperfine coupling constants of substituted cumyl monoradicals (ref. 5).

EPR SPECTROSCOPY

Electronic substituent effects on the D parameter

The D parameters of the localized triplet 1,3-diradicals **1** and **2** depend on the spin-delocalizing propensity of the aryl substituents X and Y . For convenience, we have defined the $\Delta D = D_H - D_X$ quantity [4a-c], for which positive values ($\Delta D > 0$) are characteristic for spin-accepting substituents, e.g. p -CF₃, p -CN, p -NO₂, but also p -NH₂, while negative values ($\Delta D < 0$) are observed for spin-donating substituents, e.g. p -F, p -OCOME or p -OH, but also all *meta* substituents (Table 1). The plot of the ΔD values of the monosubstituted **1** with the symmetrically disubstituted triplet diradicals **2** (Fig. 1a) shows a linear correspondence with a slope of 0.55 ($r^2 = 0.991$), which experimentally confirms convincingly the additivity of the ΔD values in such localized triplet 1,3-diradicals. Consequently, the triplet diradicals **1** and **2** may be described as a composite of two geometrically fixed cumyl radical fragments. That this approximation is justified, is evidenced by the good correlation ($r^2 = 0.934$) between the D parameters of the triplet diradicals **2** and the a_β hyperfine coupling constants of the corresponding substituted cumyl radicals [5] (Fig. 1b), as would be expected for these two EPR-spectral parameters.

Since the a_β hyperfine coupling constant is a direct measure of the α spin density (ρ_α) in cumyl radicals [5], the D parameter should also reflect changes in the α spin density of the cumyl radical fragment. A detailed theoretical analysis of the D parameter reveals that the dominant spin-spin dipolar interaction between the two radical-bearing sites depends both on the local spin densities ρ_A and ρ_B at the radical termini A and B (eq 1) and the distance d_{AB} between the A and B spin sites [4]. Thus, electronic

$$D = (3\mu_0 g^2 \beta^2 / 16\pi) \rho_A \rho_B / d_{AB}^3 \quad (\text{eq 1})$$

$$RSE = \Delta H_f(90^\circ) - \Delta H_f(0^\circ) \quad (\text{eq 2})$$

substituent effects in the triplet diradicals **2** may be assessed by evaluating the α spin densities (ρ_α) semiempirically (PM3-AUHF/CI) for the *para*- and *meta*-substituted cumyl radicals. Indeed, as displayed in Fig. 2a, the experimental D parameters of the triplet diradicals **2** correlate impressively well ($r^2 = 0.966$) with the calculated α spin densities of the cumyl monoradical model systems.

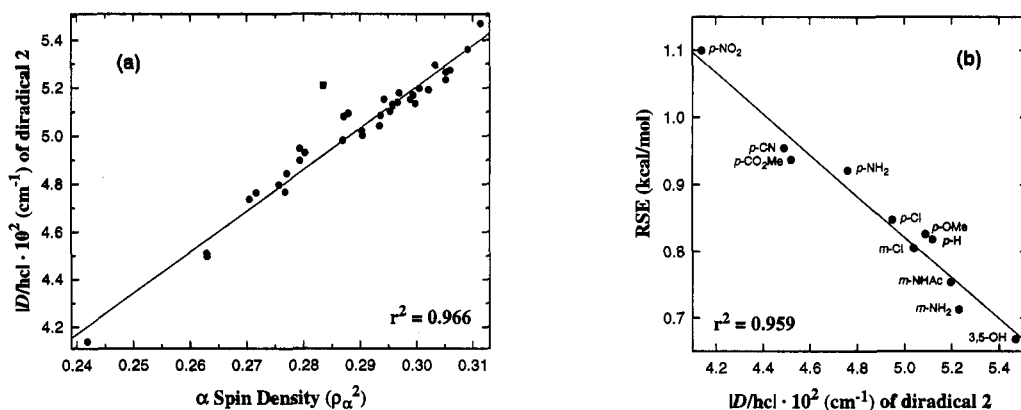


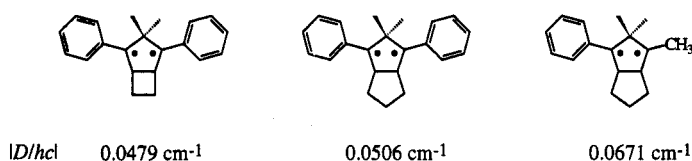
Figure 2: (a) Experimental D parameters of the triplet diradicals **2** versus the theoretical α spin density (ρ_α) of the cumyl monoradical fragments and (b) calculated RSE values of the cumyl monoradicals versus the D values of the triplet diradicals **2**.

For the benzyl and cumyl radicals [5] it has been reported that the α spin density (ρ_α) constitutes a useful probe to determine radical stabilization energies (RSE). Since we have shown that the D values of the triplet diradicals **2** correlate well with the α spin densities of the corresponding cumyl radicals, a correspondence between the substituent-promoted variations of the D parameter in the localized triplet diradicals **2** and the radical stabilization energy (RSE) in the corresponding monoradicals was expected. Such RSE values may be conveniently computed as the rotational barrier around the C-C σ bond between the aryl and radical-bearing moieties [6], given by the difference (eq 2) between the energy of the 90° (no delocalization) and the 0° (maximal delocalization) conformers [5,6]. These computations were

performed in the same way as for α spin densities (*vide supra*) and the good ($r^2 = 0.959$) correlation of the calculated RSE values with the experimental D parameters (Fig. 2b) clearly establishes that the D parameter of the localized triplet diradicals **1** and **2** reflects reliably the electronic factors which control radical stabilization in benzyl-type radicals.

Geometrical effects on the D parameter

Besides spin densities, the D parameter (eq 1) also depends on the interspin distance d_{AB} . Thus, at constant spin densities ρ_A and ρ_B , structural variations may be probed in triplet diradicals through the d_{AB} dependence. For the systems studied herein, this may be conveniently accomplished by changing the annelating ring at the 4,5 positions of the 1,3-cyclopentanediyli moiety in the diradicals **1**, which should serve as a vice to examine geometrical effects in the D parameter. For the symmetrical diphenyl-substituted derivatives (constant spin densities ρ at the radical sites), as expected, cyclobutane-bridging decreases the D parameter. This may be rationalized in terms of considerable angle widening in the



cyclopentane-1,3-diyl moiety which results in a larger distance d_{AB} and, hence, the lower D value. For comparison, substitution of a phenyl by a methyl group at the radical site in the triplet diradical leads to an increase of the D value. For the lower delocalizing ability of the methyl *versus* phenyl group, the spin density in the triplet diradical is more localized on the radical site and, hence, the higher D value [4d].

The influence of heteroaromatic π systems on the D parameter

An interesting structural modification to the benzyl/cumyl systems are the pyridylmethyl and its protonated and N -oxide derivatives. The pyridylmethyl monoradicals have been difficult to investigate by EPR spectroscopy [7a], whereas the protonated and pyridine- N -oxide radical derivatives are still unknown. For preparative reasons we prepared only the unsymmetrically substituted diradicals **3**, but the additivity relation $D_{\text{unsymm}} = \sqrt{D_{\text{parent}} \cdot D_{\text{symm}}}$ (parent \equiv diphenyl substitution) offers the opportunity to

TABLE 2: D Parameters of the Triplet Diradicals **3** ^{a)}

Het	$ D/hc $ ^{b)}	ΔD ^{c)}
4'-Pyridyl- N -oxide	0.0365	+ 1.41
2'-Thienyl	0.0391	+ 1.15
2'-Furanyl	0.0411	+ 0.95
4'-Pyridylum	0.0473	+ 0.33
2'-Pyridylum	0.0487	+ 0.19
3'-Pyridyl	0.0508	- 0.02
3'-Pyridylum	0.0512	- 0.06
2'-Pyridyl	0.0515	- 0.09
3'-Pyridyl- N -oxide	0.0516	- 0.10
4'-Pyridyl	0.0517	- 0.11
3'-Thienyl	0.0530	- 0.24
3'-Furanyl	0.0573	- 0.67

a) Measured in a MTHF glass matrix at 77 K; b) values (cm^{-1}) for the symmetrical substituted diradicals **3** calculated according to the additivity relation, error $\pm 0.0001 \text{ cm}^{-1}$; c) values (10^2 cm^{-1}) are given by $\Delta D = D_{\text{cumyl}} - D_{\text{heteroaryl}}$.

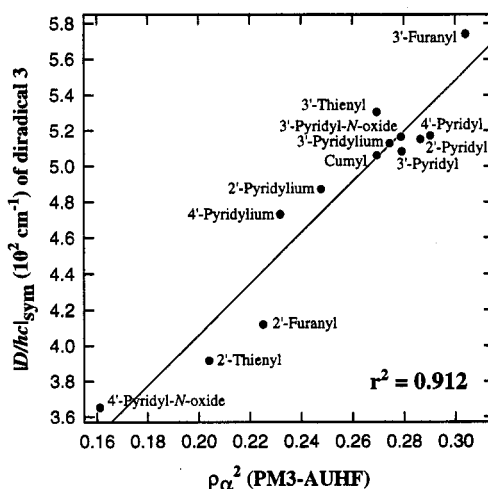


Figure 3: D parameters of the triplet diradicals **3** versus the theoretical α spin density (ρ_{α}) of the heteroaryl monoradical fragments.

calculate the corresponding D values for the symmetrical disubstituted derivatives. Besides the pyridine systems, we have extended our investigations also to 5-membered heteroaromatic π systems such as furanes and thiophenes, for which only a few of the monoradicals have been reported [7b]. The D values are collected in Table 2 and display unusual features. For example, the largest positive ΔD (+ 1.41) values is registered for the 4'-pyridyl- N -oxide derivative and, thus, constitutes the most effective spin acceptor of all aryl substituents determined so far. Moreover, the 2'-furyl and 2'-thienyl derivatives act as strong spin acceptors, whereas their 3'-isomers are definitely strong spin donors. These striking electronic effects are genuinely reproduced by semiempirical MO calculations of the spin densities for the corresponding monoradicals as displayed by the remarkable correlation in Fig. 3.

The present results demonstrate convincingly that electronic substituent effects on the α spin density (ρ_α) and radical stabilization (RSE) of benzyl-type monoradicals are reflected reliably by the D parameters of the triplet diradicals **1** and **2**. Hence, the spectroscopic ΔD scale does not suffer from the limitations (polar versus radical contributions) inherent with the popular kinetic chemical scales and provides a novel mechanistic tool to assess radical properties. The over 50 aryl substituents in Table 1 and the heteroaromatic π systems in Table 2 illustrate how successfully electronic substituent effects in π -conjugated radicals may be understood in terms of the D parameter for triplet diradicals.

LASER FLASH SPECTROSCOPY

The legitimate question arises whether the observed electronic substituent effects on the D parameters are reflected in the triplet lifetimes of these localized triplet diradicals **1** and **2**. These species were conveniently generated in the liquid phase at room temperature by direct laser-pulse excitation of the n, π^* azo chromophore in the azoalkane precursor, followed by fast ISC and deazetation to the triplet diradical [8]. The SOC matrix elements are strongly dependent on conformational and electronic effects [9,10], and for our purposes, diradicals **1** and **2** were designed to investigate solely the latter contribution. In contrast to open-chain diradicals, the planar cyclopentadienyl conformation forces the radical orbitals into a parallel orientation, which holds for the complete set of substituents. Time-resolved UV monitoring of the benzyl-type radical chromophore (ca. 320 nm) in the diradicals **1** and **2** afforded the triplet lifetimes in Table 1, for which solvent effects were found to be small.

Electron-donating substituents like p -OMe enhance ISC rates, whereas electron-accepting groups like p -CN or p -NO₂ reduce it. In fact, that the ISC rates are controlled by electronic substituent effects is evidenced by the linear dependence of ISC rates with the Hammett σ constants (Fig. 4b). The use of the σ^+ parameter for $para$ substituents gave the best results since these values are proportional to the ionization potential of the corresponding monoradicals [11] and, hence, also to SOMO energies of the corresponding benzyl monoradicals. All heavy-atom substituents (p -Br, p -I, m -I) are off-line in Fig. 4b, which demonstrates their ISC-promoting ability due to increased SOC through the heavy-atom effect.

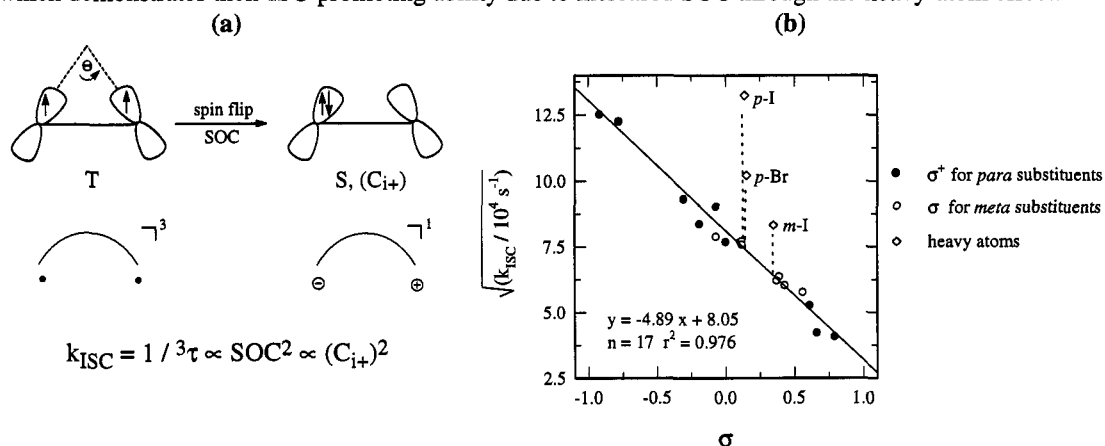


Figure 4: (a) Mechanism of spin-orbit coupling (SOC) for intersystem crossing (ISC) in triplet diradicals and (b) ISC rate constants k_{ISC} of the symmetrically substituted triplet diradicals **2** versus Hammett σ constants.

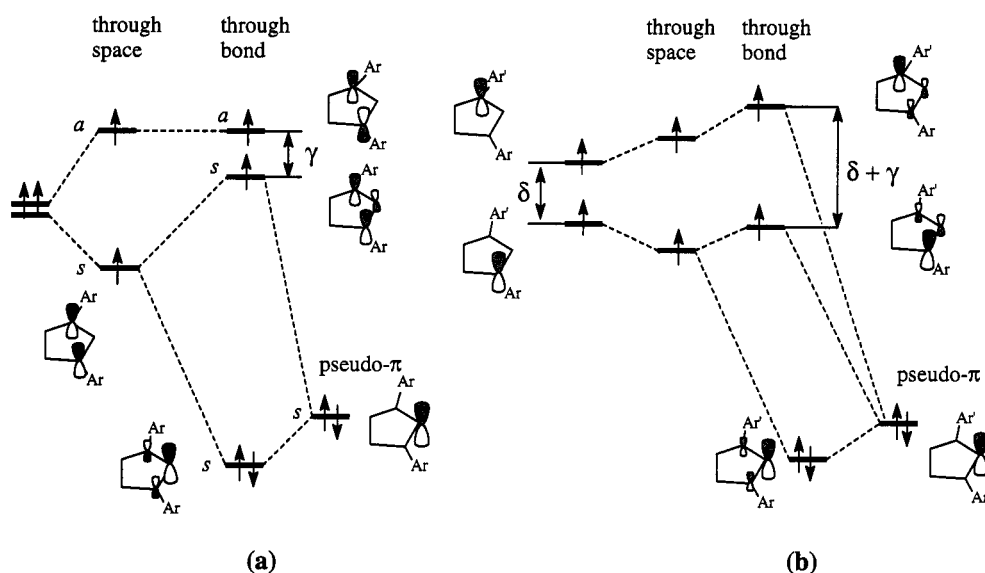


Figure 5: The orbital energy diagrams of the two NBMOs for a) *homosymmetric* and b) *unsymmetric* triplet diradicals with *through-space* and *through-bond* interactions.

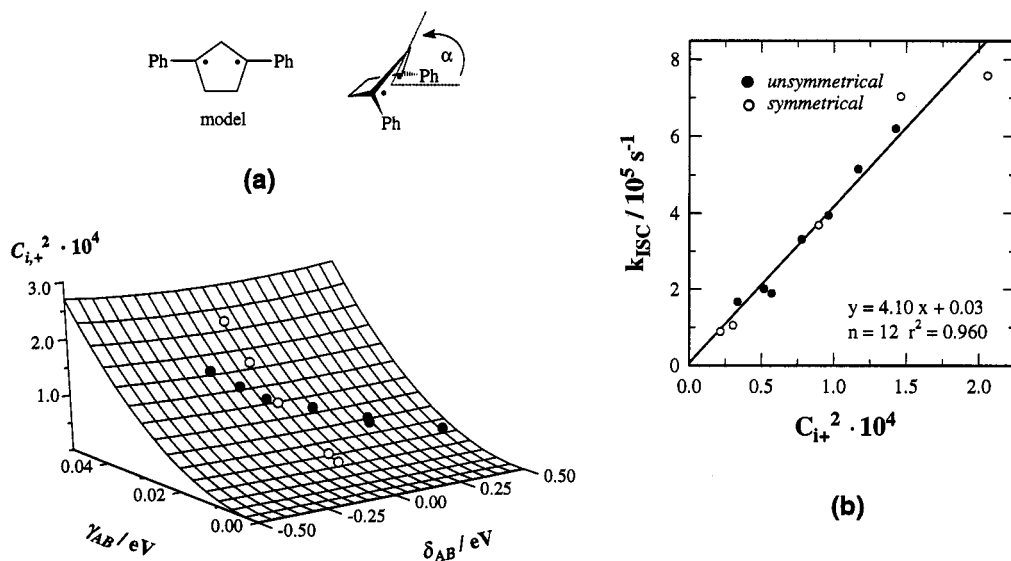


Figure 6: (a) Calculated C_{i+} coefficients, γ and δ parameters for the model system and (b) experimental ISC rate constants for diradical **1** versus the calculated C_{i+} coefficients.

The ISC process for triplet species is described by the SOC matrix, a perturbation which promotes the forbidden transition between different spin states [10]. In contrast to the D parameter, which through the dipolar spin-spin interaction constitutes a measure of the spin densities at the radical sites (eq 1), the SOC process is dominated by the covalent interactions (*through-space* and *through-bond*) between the two nonbonding molecular orbitals (NBMO) that house the diradical electrons and the relative orientation Θ of these radical orbitals [9,10]. In the two-electron-two-orbital model the one-electron-SOC matrix elements are proportional to the contribution of the ionic state ($|A^2+B^2\rangle$) in the singlet ground state of the diradical through the coefficient C_{i+} (for nomenclature and definitions see ref. 3b). A rationale is given in terms of a simple picture (Fig. 4a) for the mechanism of spin flip in a triplet diradical, which for reasons

of momentum conservation demands a simultaneous change of the orbital population. This occurs preferentially in a 90° tilt of the orbital and leads to an ionic singlet state.

We have analyzed the SOC matrix elements within the two-electron-two-orbital model [3,10]. The coefficient C_{i+} is a function of two parameters γ and δ , which are analogous to the Hückel resonance (β) the Coulomb (α) parameters [10d]. The qualitative influence of the γ and δ parameters may be deduced from the energy diagram in Figure 5 on the energy gap of the diradical NBMO's for the *homo*- and *unsymmetrical* diradical prototypes. It should be recalled that the energy gap of the two NBMO results from an imbalance of *through-space* and *through-bond* interactions. In the *homosymmetrical* case ($\delta = 0$), for lower-lying radical orbital basis energies a smaller effective γ will result. In the *unsymmetrical* case, the inherent difference in the radical orbital basis energies is manifested in δ as well as the orbital interaction in γ . Since *through-bond* interaction are included, it is more adequate to call the approximation a two-electron-2-MO model with effective γ and δ parameters.

The theoretical γ and δ parameters were computed by the AM1 method. Unfortunately, this semiempirical MO method overestimates the *through-bond* relative to the *through-space* interactions [3] and, thus, the calculations were performed on a specific diradical geometry of a model system (Fig. 6a, bent conformation with $\alpha = 27^\circ$), which compensates this artefact by enhancing the *through-space* interaction. Through substituent variation it is possible to design a set of model triplet diradicals which are described by different pairs of γ and δ parameters to probe how well the computed SOC matrix elements correlate with the experimental ISC rates. Figure 6a shows the principal functional dependence of C_{i+}^2 on the parameters δ and γ . Parameter pairs for which experimental data exist are marked. The excellent correlation ($r^2 = 0.960$) of the theoretical ionic state contribution C_{i+}^2 and the experimental ISC rates is demonstrated in Figure 6b.

In summary, the rational design of localized triplet 1,3-cyclopentenediyl diradicals **1** and **2** made it possible to probe experimentally electronic substituent effects on ISC rates. A theoretical analysis of the SOC process, the dominant mechanism on ISC in such planar cyclopentane-1,3-diyl species, revealed that substituent effects on the triplet lifetimes can be attributed to electronic *through-bond* and *through-space* interactions. In contrast, basis energy differences between the two radical sites in unsymmetrically substituted triplet diradicals have little effect on the triplet lifetimes.

HIGHER SPIN SYSTEMS

The remarkable persistence of the triplet diradicals **1** and **2** at 77 K in matrices encouraged us to employ these localized paramagnetic units as building blocks for higher spin states. The optimal ferromagnetic coupler *meta*-phenylene [12] was utilized to generate the tetradical **4** [4] and, indeed, EPR spectroscopy unequivocally confirmed its spin state to be a quintet. Spectral simulation, which required inclusion of fourth-order terms, afforded the zero-field splitting parameters $|D| = 0.00955 \text{ cm}^{-1}$ and $|E| = 0.0029 \text{ cm}^{-1}$. Kinetic measurements of the EPR intensity on the tetradical proved it to be astonishingly persistent with a half-life of 55 h at 77 K, which is even twice that of the corresponding diradicals **1**.

A very sensitive dependence on the UV wavelengths was found during the generation of the tetradical **4** from the bis-azo precursor. Irradiation with the monochromatic 364-nm laser line afforded only the corresponding diradical species (monodeazetation), whereas the 333-nm laser line led to the desired quintet tetradical **4**. However, irradiation of freshly generated tetradical **4** at 351-nm photobleached the quintet EPR signal. Such photochemically induced intersystem crossing has not been observed so far for higher spin species.

In conclusion, the quintet spin state of tetradical **4** represents the first example of a tetradical based on two localized 1,3-cyclopentenediyl units, not only with interesting electron paramagnetic behavior but also with unexpected optical features. These novel results open up the opportunity to devise persistent organic ferromagnetic materials, which may act as wavelength-sensitive optical switches.

Acknowledgement

We are grateful for generous financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for a Kekulé fellowship (1992-94) to W.M.N..

Literature

- [1] a) F. D. Coms, D. A. Dougherty, *Tetrahedron Lett.* **29**, 3753 (1978). b) W. Adam, G. Reinhard, H. Platsch, J. Wirz, *J. Am. Chem. Soc.* **112**, 4570 (1990).
- [2] a) D. A. Dougherty in *Kinetics and Spectroscopy of Carbenes and Triplet Biradicals*; M. S. Platz (ed.) Plenum Press: New York, (1990), p- 117-142; b) S. P. McGlynn, T. Azumi, M. Kinoshita in *Molecular Spectroscopy of the Triplet State*, Prentice Hall, Englewood Cliffs, N. J. (1969).
- [3] a) W. Adam, L. Fröhlich, W. M. Nau, J. Wirz, *J. Am. Chem. Soc.* **115**, 9824 (1993). b) F. Kita, W. M. Nau, W. Adam, J. Wirz, *J. Am. Chem. Soc.* **117**, 8670 (1995).
- [4] a) W. Adam, L. Fröhlich, W. M. Nau, H.-G. Korth, R. Sustmann *Angew. Chem. Int. Ed. Engl.* **32**, 1339 (1993). b) W. Adam, H. M. Harrer, F. Kita, W. M. Nau, *Pure Appl. Chem.* in press. c) W. Adam, C. van Barneveld, S. E. Bottle, H. Engert, G. R. Hanson, H. M. Harrer, C. Heim, W. M. Nau, D. Wang, *J. Am. Chem. Soc.* **118**, 3974 (1996). d) W. Adam, H. M. Harrer, T. Heidenfelder, T. Kammel, F. Kita, W. M. Nau, C. Sahin, *J. Chem. Soc. Perkin Trans. 2* (1996) in press.
- [5] D. R. Arnold in *Substituent Effects in Radical Chemistry*; H. G. Viehe, Z. Janousek, R. Merényi (ed.); Reidel & Dordrecht, Netherlands, NATO ASI ser., Ser. C, (1986), Vol. 189, p. 171-188.
- [6] a) A. E. Dorigo, Y. Li, K. N. Houk, *J. Am. Chem. Soc.* **111**, 6942 (1989). b) F. G. Bordwell, X.-M. Zhang, M. S. Alnajjar, *J. Am. Chem. Soc.* **114**, 7623 (1992). c) D. A. Hrovat, W. T. Borden, *J. Phys. Chem.* **98**, 10460 (1994).
- [7] a) R. A. Jackson, C. J. Rhodes, *J. Chem. Soc., Perkin Trans. 2* 121 (1985). b) R. J. Waltman, A. C. Ling, J. Bargon, *J. Magn. Res.* **48**, 93 (1982).
- [8] W. Adam, G. Fragale, D. Klapstein, W. M. Nau, J. Wirz, *J. Am. Chem. Soc.* **117**, 12579 (1995).
- [9] a) R. A. Caldwell in *Kinetic and Spectroscopy of Carbenes and Biradicals*; Platz, M. S. (ed.) Plenum: New York (1990), p 117. b) W. Adam, S. Grabowski, M. R. Wilson, *Acc. Chem. Res.* **23**, 165 (1990).
- [10] a) L. Salem, C. Rowland, *Angew. Chem.* **84**, 86 (1972); *Angew. Chem. Int. Ed. Engl.* **11**, 92 (1972). b) V. Bonacić - Koutecký, J. Koutecký, J. Michl, *Angew. Chem.* **99**, 216 (1987); *Angew. Chem. Int. Ed. Engl.* **26**, 170 (1987). c) J. Michl, *J. Am. Chem. Soc.* **118**, 3568 (1996). d) A. Streitwieser in *Molecular Orbital Theory for Organic Chemists*, J. Wiley & Sons, New York/London (1961).
- [11] D. D. M. Wayner, B. A. Sim, J. J. Dannenberg, *J. Org. Chem.* **56**, 4853 (1991).
- [12] A. Rajka, *Chem. Rev.* **94**, 871 (1994).