Photochemically generated cyclopentane-1,3-diyl triplet diradicals as model systems for the assessment of spin delocalization in heteroaryl-substituted benzyl-type monoradicals through the EPR spectral *D* parameter

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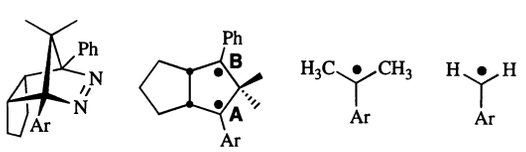
The zero-field *D* parameters of a comprehensive set of cyclopentane-1,3-diyl triplet diradicals 2 were determined at 77 K in a 2-MTHF glass matrix. The *D* values were found to be dependent on the heteroaryl substituents in the decreasing order 3-furyl ≫ 3-thienyl > 4-pyridyl ≈ 3-*N*-oxypyridyl > 2-pyridyl ≈ 3-pyridylium > 3-pyridyl ≈ phenyl ≫ 2-pyridylium ≫ 4-pyridylium ≫ 2-furyl ≫ 2-thienyl ≫ 4-*N*-oxypyridyl. Good linear correlations were obtained with the reported a_α coupling constants (r^2 = 0.953) for the benzyl monoradicals 4 and with the semiempirically calculated (PM3) α spin densities (r^2 = 0.928) for the cumyl monoradicals 3. To rationalize the observed electronic effects, for convenience the ΔD_{Ar} scale was defined as a measure of the spin-delocalizing ability of the different heteroaryl substituents relative to the phenyl group as reference. The hitherto unknown electronic effects of *N*-oxidation and protonation for the different pyridyl regioisomers as well as the regioisomeric effects of the furyl and thienyl substituents, are experimentally reflected accurately by the changes in the *D* parameter of the triplet diradicals 2 and explained theoretically with the help of MO calculations for the corresponding monoradicals 3.

Introduction

The photochemical deazetation of diazabicyclo[2.2.1]heptane (DBH) derivatives generates conveniently cyclopentane-1,3-diyl triplet diradicals, which are persistent in low-temperature matrices.[1] These intermediates may be detected by EPR spectroscopy and characterized by the zero-field splitting (zfs) parameters *D* and *E*.[1] For such localized triplet 1,3-diradicals, the *D* parameter derives from a two-centre dipolar interaction between the radical termini, whose magnitude depends on the interspin distance d_{AB} and the spin densities ρ_A and ρ_B at the respective radical sites A and B [eqn. (1)]. The spin density[2a,b] as

$$D = \frac{3\mu_0 g^2 \mu_B^2}{16\pi}\left(\frac{\rho_A \rho_B}{d_{AB}^3}\right) \qquad (1)$$

well as the geometry dependence[2c] have recently been confirmed experimentally and theoretically. Therefore, such localized 1,3-disubstituted cyclopentane-1,3-diyl triplet diradicals can be considered as a composite of two geometrically fixed benzyl-type monoradicals. Hence, at constant d_{AB}, the *D* parameter is a sensitive probe for electronic substituent effects through the α spin density dependence and provides a measure of radical stabilization through spin delocalization.



1 **2** **3** **4**

An interesting electronic modification of the well-studied benzyl (and cumyl) radicals **4f**[3] are the pyridylmethyl derivatives **4g**,**i**,**k**.‡ However, their accurate EPR spectral examination has been difficult because insufficiently high concentrations of these radicals could be obtained in solution, while the additional structural complexity has encumbered the reliable assignment of coupling constants even in computer-aided analyses.[4] Hence, the effects on the spin density distribution in such species has remained doubtful. For example, the assignment of the a_α hyperfine coupling constants for the pyridylmethyl radicals **4** in solution,[4] which are a direct measure of the α spin density (McConnell equation),[1b] showed considerable disagreement with results obtained for these radicals in adamantane matrices.[5] However, all pyridylmethyl radicals showed larger a_α hfc constants (*cf.* Table 1) than the parent benzyl case, *i.e.* 4- > 2- > 3-pyridylmethyl > benzyl, which was also in line with β muon couplings of muonated aryl-substituted ethyl radicals.[6] Semiempirical calculations have failed so far to account for these experimental results.[5,7]

Of relevance in this context are also the thienyl- and furylmethyl radicals **4b–c** and **l–m**, since they constitute five-membered ring heteroaromatic analogues of the parent benzyl radical. Of these, only the radicals **4b–c** and **l** have been studied by EPR spectroscopy in solution and shown to exhibit also complex spectra. The a_α hfc constants[8] differ strongly from those of the benzyl radical (*cf.* Table 1), which is especially the case for the *ortho* isomers. Moreover, these electronic substituent effects have not been rationalized in terms of spin delocalization by these heteroaryl groups.

In view of the aforementioned inconsistencies, it was of interest to examine the electronic influence of the various regioisomeric pyridyl-, furyl- and thienyl-methyl substituents on the *D* parameter in the triplet 1,3-diradicals **2**. Specifically, it was to be assessed whether the α spin density at the radical site serves as a measure of the spin-delocalizing propensity of these heteroaryl units. Since the *D* parameter derives solely from the dipolar spin–spin interactions,[2a] this quantity is not encumbered by hyperfine splittings at the radical site in the EPR spectra, which should facilitate the diagnosis of substituent effects. Herein, we report the results of our investigation for the unsymmetrical mono-substituted diradicals **2**, also for the

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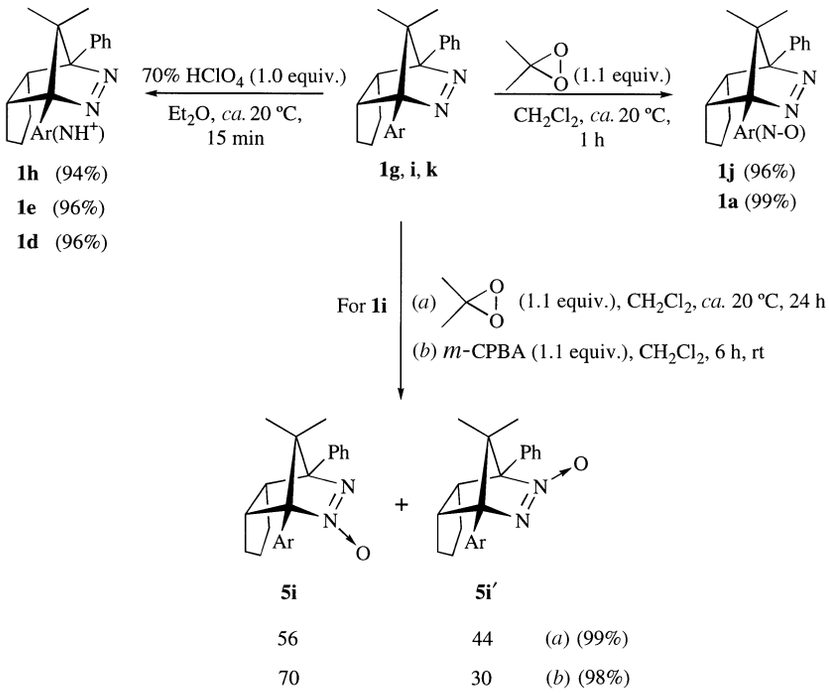
‡ For the various substituents of Ar (**a**–**m**) of compounds **1**–**5** see Table 1.



Scheme 1 Preparation of the pyridinium derivatives **1d**,**e** and **h** and the pyridine-*N*-oxide derivatives **1a** and **j**

protonated and *N*-oxidized pyridylmethyl derivatives, the latter examined EPR-spectrally for the first time. We demonstrate unequivocally that the *D* parameter is a reliable measure of the spin-delocalizing properties of heteroaryl π systems.

Results

The synthesis of the heteroaryl-substituted azoalkanes **1b–c**,**g**,**i** and **k–m** was carried out according to literature procedures,[9a,b] whereas the derivative **1f** has been reported earlier.[9c] The pyridyl-substituted azoalkanes **1g**,**i** and **k** were further functionalized by nitrogen protonation and oxidation (Scheme 1). Thus, with 70% perchloric acid they gave the pyridinium perchlorates **1d–e** and **h** in excellent yields, while the *N*-oxides **1a** and **1j** were obtained by dimethyldioxirane oxidation.[10] Unfortunately, the oxidation with (*a*) dimethyldioxirane or (*b*) *m*-CPBA of the *ortho* regioisomer **1i** did not result in the desired *N*-oxide, instead the two azoxy derivatives **5i** and **i′** were formed in high yields (*cf.* Scheme 1).

The diradicals **2** were generated in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K by means of irradiation with the 364 nm line of an argon ion laser and a representative EPR spectrum is given in Fig. 1. The results of the EPR measurements are summarized in Table 1. A marked dependence of the experimental *D* values on the heteroaryl substituent is evident, which is in general larger than the previously observed electronic effects of *para* and *meta* substituents on the phenyl derivative **2f**.[2] Hence, the smallest *D* value is displayed by the diradical **2a** (0.0430 cm^{-1}), whereas diradical **2m** possesses the largest (0.0539 cm^{-1}) and both flank the parent phenyl case **2f** (0.0506 cm^{-1}), which is taken as a reference system for these heteroaryl substituents. While the *meta*-pyridyl regioisomer **2g** (0.0507 cm^{-1}) has the same *D* value within the experimental error as the phenyl reference system **2f** (0.0506 cm^{-1}), both the *ortho*-**2i** (0.0510 cm^{-1}) and *para*-**2k** (0.0512 cm^{-1}) regioisomers exhibit definitely larger values.

More dramatic effects are witnessed for the thienyl (**2b**,**l**) and furyl (**2c**,**m**) derivatives. Thus, the *ortho* isomers **2b** (0.0445 cm^{-1}) and **2c** (0.0457 cm^{-1}) of these five-membered heteroaryl substituents have substantially smaller *D* values than the reference system **2f** (0.0506 cm^{-1}). However, the *meta* isomers **2l** (0.0518 cm^{-1}) and **2m** (0.0539 cm^{-1}) possess larger *D* values.

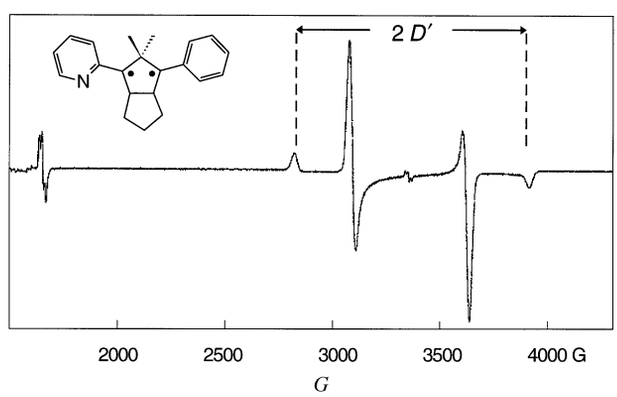
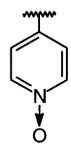
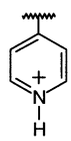
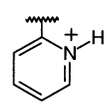
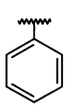
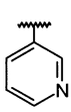
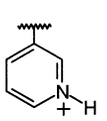
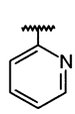
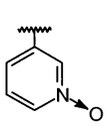
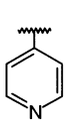
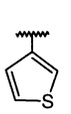
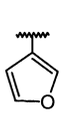


Fig. 1 Representative EPR spectrum of the triplet diradical **2i**. The important *Z* signals for the determination of the *D* parameter are also indicated.

Functionalization (nitrogen protonation and oxidation) of the pyridine lone pair affects significantly the *D* parameter of the corresponding diradicals **2**. This is best exemplified for the *para*-pyridyl regioisomer **2k** (0.0512 cm^{-1}), for which the *D* value decreases substantially on protonation to afford the diradical **2d** (0.0489 cm^{-1}). A similar trend, but less pronounced, applies to the *ortho* regioisomers, *i.e.* **2i** (0.0510 cm^{-1}) *versus* **2e** (0.0496 cm^{-1}). For the corresponding *meta* derivatives **2g** (0.0507 cm^{-1}) *versus* **2h** (0.0509 cm^{-1}), the effect of protonation is nominal, if at all significant. Contrary to the *ortho* and *para* regioisomers, the *D* parameter is displaced to slightly larger values.

N-Oxidation is substantially more effective than protonation in changing the *D* parameters and, hence, the electronic properties of the pyridine ring. Thus, the *para*-*N*-oxide **2a** (0.0430 cm^{-1}) stands out of all heteroaryl substituents investigated here with the smallest *D* value and implies some dramatic electronic changes. In contrast, for the *meta* regioisomer **2j** (0.0511 cm^{-1}) a small but definite displacement to a higher *D* value is observed on *N*-oxidation of the pyridyl derivative **2g** (0.0507 cm^{-1}). These electronic effects of the heteroaryl substituents shall now be interpreted in terms of their spin-delocalizing propensity with respect to the parent phenyl derivative **2f** as reference system.

Table 1 Experimental D values of the triplet diradicals **2**, calculated α spin densities of the cumyl-type monoradicals **3**, ΔD_{Ar} values for the heteroaryl substituents and a hyperfine coupling constants of the corresponding benzyl-type monoradicals **4**

	Ar	$\lvert D/hc\rvert$/cm^{-1} [a]	ρ_α of **3** [b]	$\Delta D_{Ar}/10^2$ cm^{-1} [c]	a_α of **4**/G
2a		0.0430	0.423	+0.76	—
2b		0.0445	0.452	+0.61	13.84 [e]
2c		0.0457	0.475	+0.49	13.85 [e]
2d		0.0489	0.469	+0.17	—
2e		0.0496	0.498	+0.10	—
2f		0.0506 [d]	0.522	0.00	16.35 [f]
2g		0.0507	0.538	−0.01	16.51 [g]
2h		0.0509	0.524	−0.03	—
2i		0.0510	0.544	−0.04	16.80 [g]
2j		0.0511	0.532	−0.05	—
2k		0.0512	0.551	−0.06	17.20 [g]
2l		0.0518	0.519	−0.12	16.73 [e]
2m		0.0539	0.552	−0.33	—

[a] Measured in a 2-MeTHF matrix at 77 K, error ±0.0001 cm^{-1}, $\lvert E/hc\rvert$ < 0.002 cm^{-1}. [b] Calculated α spin densities, *cf.* text. [c] Calculated according to eqn. (2). [d] Ref. 2. [e] Ref. 8, stated error ±0.03 G. [f] Ref. 3, stated error ±0.02 G. [g] Ref. 4, stated error ±0.01 G.

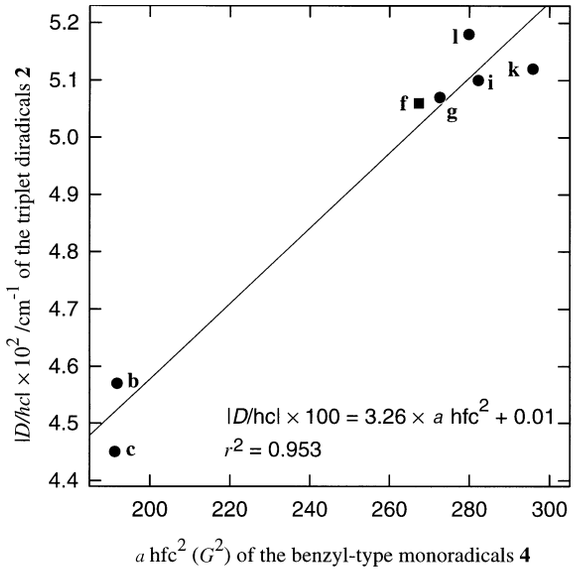


Fig. 2 D values of the triplet diradicals **2** *versus* the experimental a hyperfine splitting constants of the benzyl-type monoradicals **4** taken from refs. 3, 4 and 8; (■) marks the phenyl reference system **2f**/**4f**

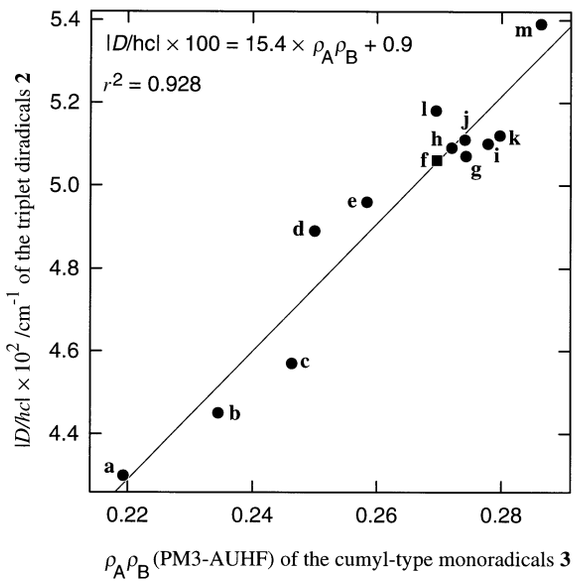


Fig. 3 D values of the triplet diradicals **2** *versus* the calculated α spin densities (ρ_α) of the cumyl-type radicals **3**; (■) marks the phenyl reference system **2f**/**3f**

Discussion

The radical centres in the localized triplet 1,3-diradicals act independently of each other, except for dipolar spin–spin interactions, as confirmed through the additivity of substituent effects in 1,3-diaryl-substituted derivatives.[2] Since in all unsymmetrical derivatives **2** one radical side is kept constant (phenyl substitution), the experimentally assessed changes in the D parameter must derive from the different heteroaryl substituents **a**–**m**. This is experimentally verified by the good linear correlation between the reported a hyperfine couplings of the monoradicals **4** and the D parameters of the triplet diradicals **2** in Fig. 2. Hence, the two EPR spectroscopic $\lvert D/hc\rvert$ and a hfc quantities manifest that the spin-delocalizing propensity of the heteroaryl substituents decrease in the order 2-thienyl > 2-furyl > phenyl > 3-pyridyl > 2-pyridyl > 4-pyridyl > 3-thienyl > 3-furyl.

Indeed, theoretical spin densities, calculated by the semiempirical PM3 method for the heteroaryl-substituted monoradicals **3**, confirm the above trend (Fig. 3).[5,7] Consequently, the

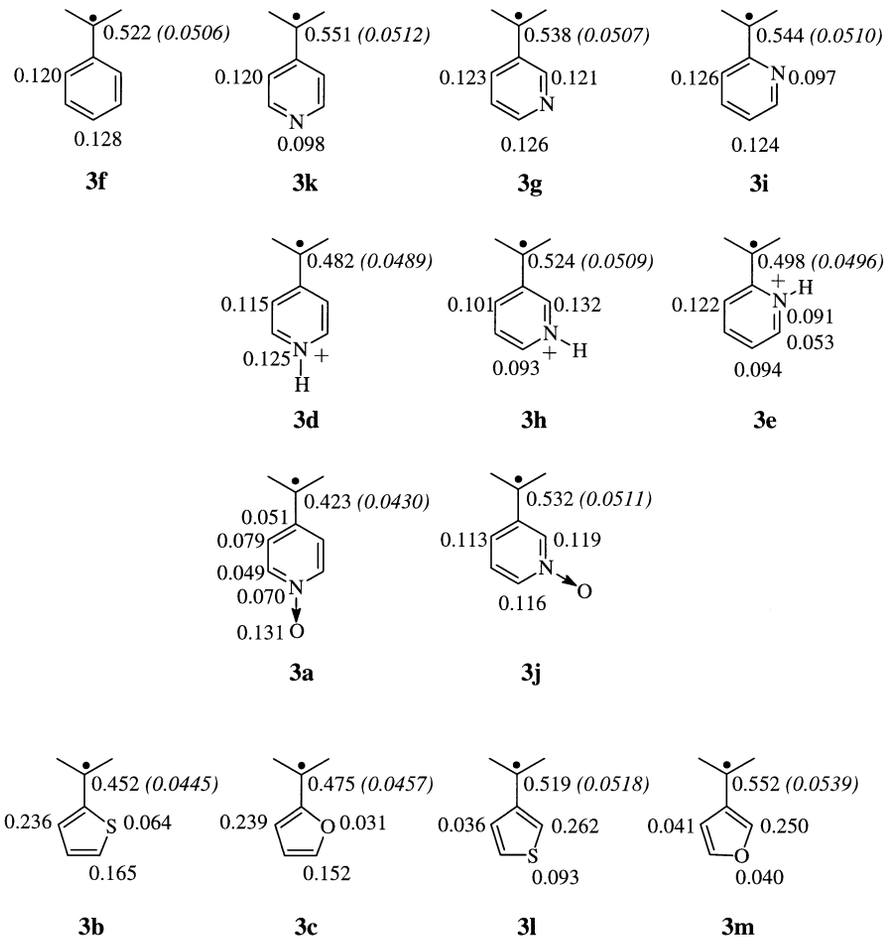


Fig. 4 Calculated (PM3-AUHF) spin densities (ρ) for the cumyl-type monoradicals **3** and experimental D parameters of the triplet diradicals **2** (values given in parentheses)

good correlation of the D parameters for the triplet diradicals **2** with the experimental hyperfine coupling constants (Fig. 2) and the calculated a spin densities (Fig. 3) of the corresponding monoradicals **3** demonstrate that electronic substituent effects for heteroaryl groups are reliably reproduced by the D values in terms of spin delocalization. The better the heteroaryl substituent delocalizes spin, the more spin diffuses into the aromatic moiety (mainly at the *ortho* and *para* positions) and less spin resides at the radical centre and a lower D value results, as demanded by eqn. (1).

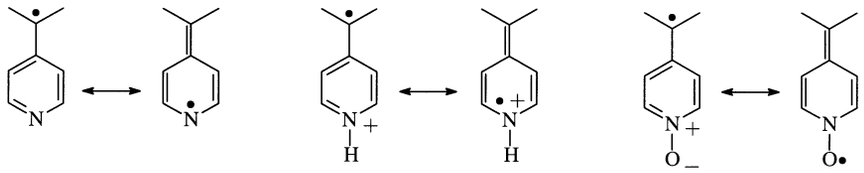
The D values in Table 1 display some interesting and remarkable trends in the spin-delocalizing ability of the heteroaryl substituents. These experimental data, which have been for the first time acquired and provide a quantitative measure of heteroaryl conjugation, shall now be compared with the phenyl group as reference point. For this purpose it is convenient to define the ΔD_{Ar} parameter [eqn. (2)] as the difference between the D

$$\Delta D_{Ar} = [D_{Ph} - D(\mathbf{2})] \times 100 \qquad (2)$$

values of the phenyl (D_{Ph}) and the heteroaryl group [D(**2**)] in the triplet diradicals **2**. Thus, positive ΔD_{Ar} values indicate that the heteroaryl substituent delocalizes spin better than the phenyl group and may be classified as *spin acceptor*. Heteroaryl substituents with negative ΔD_{Ar} values delocalize spin worse than the phenyl group and may be classified as *spin donors*.

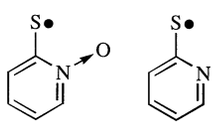
Let us first consider the three regioisomeric pyridyl-substituted triplet diradicals **2g** (−0.01), **2i** (−0.05) and **2k** (−0.06), for which the ΔD_{Ar} values are given in parentheses. Clearly, within the experimental error, the pyridyl substituent in the *meta* isomer **2g** conjugates about as well as the phenyl group, but in the *ortho* and *para* isomers **2i** and **k** delocalization is definitely less effective. This trend is also evident in the calculated spin densities (ρ_α) at the radical site of the corresponding heteroaryl-type cumyl radicals **3g** (0.538), **3i** (0.544) and **3k** (0.551) *versus* the parent phenyl reference system **3f** (0.522). Again, relative to phenyl, the pyridyl derivatives act as spin donors by enhancing the spin density at the radical site, although the effects are relatively small. Furthermore, inspection of the spin distribution within the aromatic ring of the monoradicals **3** (Fig. 4) reveals that for the more effective spin donors *ortho*- and *para*-pyridyl, the respective spin densities at the nitrogen sites, namely **3i** (0.097) and **3k** (0.098), are substantially reduced compared to those of the parent cumyl radical **3f** (0.120 at *ortho* and 0.128 at *para*). This indicates that aminyl-type radical structures such as in the resonance hybrid **A**, exemplified for the *para*-pyridyl case, are discouraged due to unfavourable spin accumulation at the nitrogen atom. This aminyl-type radical destabilization, a well documented fact,[11a] expresses itself in the reluctance of the *para*- and *ortho*-pyridyl substituents to delocalize spin into the aromatic ring in the order *para* (**3k**) > *ortho* (**3i**) > *meta* (**3g**) ≈ phenyl (**3f**). Note in Fig. 4 that for the *meta*-pyridyl derivative **3g** the *ortho* and *para* ring spin densities are essentially the same as those for the parent cumyl case **3f**. Thus, in this regioisomer the pyridyl substituent is as effective in delocalizing spin as the phenyl group because no unfavourable aminyl-type radical structures apply.

Protonation of the nitrogen atom in the pyridine moiety changes substantially its spin-delocalizing propensity. This is most prominently seen for the former weakly spin-donating *para*-pyridyl substituent in **2k** ($\Delta D_{Ar} = -0.06$), which becomes now a relatively good spin-accepting one in **2d** ($\Delta D_{Ar} = +0.17$).



A **B** **C**

This may be rationalized in terms of the stabilizing nitrogen-centred radical–cation resonance structure **B** for the monoradical **3d**, a stabilization that also applies for the *ortho*-pyridyl substituent in **3e**. Still more dramatic changes of the experimental *D* values result from *N*-oxidation, as exemplified for the 4-*N*-oxypridyl substituent in the triplet diradical **2a**. The ΔD_{Ar} value of +0.76, the largest in the set of heteroaryl substituents examined herein (Table 1), indicates massive spin delocalization into the aromatic ring. The semiempirical MO calculations for the monoradical **3a** make evident that the nitroxide resonance hybrid **C** is significantly populated, as expressed by the large spin density at the nitroxide functionality (Fig. 4). This nicely accounts for the observed strong spin-delocalizing ability of this heteroaryl substituent. A similar explanation was given recently for the *N*-oxypyridyl-2-thio radical **5a**, which adds considerably slower to dienes compared to the non-oxidized pyridyl-2-thio radical **5b**.[12] The corresponding nitroxide reson-



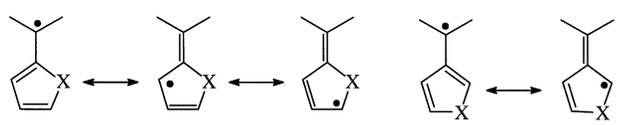
5a **5b**

ance structure for the *N*-oxide radical reduces the α spin density at the sulfur radical site and, hence, lowers the reactivity.

Additional experimental evidence for the nitroxide structure in the resonance hybrid **C** provides the *g* values of the diradicals **2**. Normally these fall in the range of 2.0020 to 2.0025, but for the triplet diradical **2a** a substantial increase to 2.0045 is found, which definitively expresses significant nitroxide radical character, since the latter have *g* values in the range from 2.0055 to 2.0065.[11b] In this context it is relevant to note that for the triplet diradical **2j** with the *meta*-*N*-oxypyridyl substituent a normal *g* value of 2.0027 is observed. This is expected because in the *meta*-*N*-oxypyridyl group the *N*-oxide functionality is not in direct conjugation with the radical centre.

The comparison of the ΔD_{Ar} parameters of the unfunctionalized, pyridyl-substituted triplet diradicals **2g** (−0.01), **2i** (−0.04) and **2k** (−0.06) with the furyl derivatives **2c** (+0.49) and **2m** (−0.33) and the thienyl ones **2b** (+0.61) and **2l** (−0.12) makes clearly evident that the five-membered ring heteroaryl substituents interact much more strongly with the radical centre. In view of the lower aromatic character of the five- *versus* the six-membered aryl substituents, the 6π electron system of the former is more easily perturbed by spin delocalizing effects.[13] Also the calculated spin densities (ρ_α) at the radical sites for the furyl and thienyl derivatives (Table 1) bring out this trend in that the changes in ρ_α are more pronounced in the five- *versus* six-membered heteroaryl substituents. Notable is the fact that the ring spin densities at the oxygen and sulfur atoms are quite low, which implies relatively little interaction of the heteroatom with the spin centre.

Interestingly, the ΔD_{Ar} parameters of the furyl- and thienyl-substituted triplet diradicals **2** vary strongly with the substitution pattern. The heteroaryl substituents in the *ortho* isomers **2b** (+0.67) and **2c** (+0.49) are much better spin delocalizers, whereas in the *meta* isomers **2l** (−0.12) and **2m** (−0.33) these heteroaryl substituents delocalize spin worse than the phenyl group in the parent triplet diradical **2f**. This is particularly well illustrated by the ring spin densities of the corresponding monoradicals **3** (Fig. 4). Almost 40% resides at the 3 and 5 positions in the *ortho* regioisomers **3b** and **c**, *ca.* 25% at the 2 positions of the *meta* derivatives **3l** and **m**. Thus, *versus* the phenyl group, the *ortho* regioisomers **3b** and **c** qualify as strong spin acceptors, while the *meta* ones operate as moderate spin donors. Why? As the theoretical ring spin densities (Fig. 4) substantiate, for the *ortho* isomers **3b** and **c** an extended pentadienyl-type spin delocalization applies in terms of the resonance structures **D** and **F**. Thus, the synergistic effect of rad-



X = S **D** **E**

X = O **F** **G**

ical and ring conjugation provides for extensive delocalization. The reason why this is much more effective than for the phenyl group is apparently, as already stated, the less pronounced aromatic character of the furyl and thienyl moieties.[13] In contrast, for the *meta* derivatives **3l** and **m**, cross-conjugation between the aromatic ring (Hückel-type) and the radical site (allyl-type) compete and spin delocalization is significantly less effective for these heteroaryl substituents relative to the phenyl group. This must not be construed that there is no spin delocalization in the *meta* regioisomers **3l** and **m** at all. Indeed, substantial (*ca.* 25%) spin density diffuses into the heteroaryl ring through allylic conjugation, as the calculated ring spin densities at the 2-positions, namely **3l** (0.262) and **3m** (0.250), portray unmistakenly; however, we reiterate that compared to the phenyl group, the 3-furyl and 3-thienyl substituents delocalize spin density in cumyl-type radicals **3** (triplet diradicals **2**) less efficiently. In fact, a better comparison of these heteroaryl substituents would be with the cyclopentadienyl anion as reference system, but all synthetic efforts on the corresponding triplet diradical have failed so far. Nevertheless, we anticipate that the delocalized negative charge in the cyclopentadienyl anion moiety would resist spin delocalization from the radical site into the aromatic ring. Consequently, the uncharged 2-furyl and 2-thienyl groups should act as spin acceptors relative to the cyclopentadienyl anion as reference group.

Our data on the *D* parameters (Table 1) for the heteroaryl-substituted triplet diradicals **2** and the theoretical spin densities for the corresponding heteroaryl derivatives of the cumyl-type monoradicals **3** (Fig. 4) have allowed us for the first time to probe experimentally and theoretically the electronic effects of pyridyl, furyl and thienyl groups on cumyl-related radical centres through spin delocalization effects. Some unprecedented electronic trends have become evident through nitrogen protonation and oxidation in the pyridine series **2g**,**i**,**k** and regioisomeric effects in the furan and thiophene derivatives **2c**,**m** and **2b**,**l**. While in principle such information may be acquired through EPR hyperfine couplings on the monoradicals,[1b,4,8] the synthetic ease of preparing the required azoalkane precursors[2,9] for the photochemical generation of the matrix-

isolated triplet diradicals and the convenience of measuring the EPR spectra for the latter,[1a,2] offers definite advantages for the herein presented methodology to assess electronic substituent effects in radical species.

Experimental

Computations

Full geometry optimization of the monoradicals **3** was carried out on the highest molecular symmetry with a planar arrangement of the aryl groups at the radical site by using the PM3 method[14a] and the A(nnihilated) UHF wave function,[14b] which are provided in the VAMP5.0 program[15] and run on an IRIS INDIGO Silicon Graphics Workstation. The a spin densities were determined with a single-point CI calculation, which results in excellent spin expectation $\langle S^2 \rangle$ values between 0.76 and 0.78 for these radicals.

EPR spectroscopy

A sample (*ca.* 5×10^{-4} mmol) of the azoalkanes **1** was dissolved in 0.3 cm^3 of MTHF, placed into an EPR sample tube (inner diameter *ca.* 2 mm) and thoroughly degassed by purging with argon gas. The sample was sealed and the matrix was prepared at 77 K by freezing the samples in liquid nitrogen. The triplet diradicals **2** were generated by irradiation with the 364 nm line of an INNOVA-100 CW argon-ion laser (widened beam, 1.5 W, 2 min) at 77 K. Their EPR spectra were recorded with a Bruker ESP-300 spectrometer (9.43 GHz, spectra accumulation with the Bruker 1620 data system, $n \geqslant 5$). The D values were determined by a manual analysis of the Z signals.[2]

General aspects

^{1}H and ^{13}C NMR spectra were measured on a Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz) spectrometer with deuteriochloroform or deuterioacetonitrile as internal standard. J values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1420 ratio recording IR spectrophotometer. UV spectra were taken on an Hitachi U 3200 spectrophotometer. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. Melting points were taken on a Büchi apparatus B-545. TLC analyses were conducted on precoated silica-gel foils Polygram SIL G/UV_{254} (40 × 80 mm) from Macherey & Nagel. Spots were identified under a UV lamp or by exposure to iodine vapour. Silica gel (63–200 μm; Woelm) was used for column chromatography, the adsorbant : substrate ratio was *ca.* 100 : 1.

Preparation of the azoalkanes 1b–c,g,i and k–m

The corresponding unsaturated azoalkane[9b] (0.500 mmol) was dissolved in ethyl acetate (40 cm^3) and *ca.* 10 mg of palladium on charcoal catalyst were added. The suspension was deareated and saturated with hydrogen gas. The hydrogenation was carried out at *ca.* 20 °C for 24 h by using a slight pressure of hydrogen gas. The catalyst was removed from the reaction mixture by filtration and the solvent evaporated (*ca.* 40 °C/15 Torr) to afford the azoalkane **1**.

(1α,4α,4aα,7aα)-4,4a,5,6,7a-Hexahydro-8,8-dimethyl-1-(2′-thienyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1b). Colourless needles (157 mg, 95%), mp 109–110 °C (decomp.) (Found: C, 74.42; H, 7.18; N, 8.44; S, 9.82. $C_{20}H_{22}N_2S$ requires C, 74.49; H, 6.87; N, 8.69; S, 9.94%); $\lambda_{max}(C_6H_6)$/nm 362 (log ε 2.09); ν_{max}(KBr)/cm^{-1} 3100, 2990, 2940, 1700, 1490, 1460; $\delta_H(CDCl_3)$ 0.27 (3 H, s, *endo*-CH_3), 1.03 (3 H, s, *exo*-CH_3), 1.58 (6 H, m, CH_2), 3.32 (1 H, dt, ^3J 8.4, ^3J 8.0, ^3J 5.0, 7a-H), 3.48 (1 H, m_c, 4a-H), 7.16 (1 H, dd, ^3J 5.0, ^3J 3.6, 4′-H), 7.34 (1 H, dd, ^3J 3.6, ^4J 1.1, 3′-H), 7.40 (4 H, m, 5′-H and Ph), 7.78 (2 H, dt, ^3J 6.7, ^4J 1.7, *ortho*-H_{phenyl}); $\delta_C(CDCl_3)$ 17.0 (q), 17.8 (q), 25.5 (t), 25.7 (t), 28.4 (t), 48.7 (d), 51.7 (d), 66.1 (s), 96.8 (s), 98.1 (s), 124.8 (d), 125.3 (d), 127.1 (d), 127.4 (2 × d), 127.8 (d), 128.3 (2 × d), 129.5 (s), 135.9 (s).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(2′-furyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1c). Colourless needles (137 mg, 89%), mp 67–68 °C (decomp.) (Found: C, 78.15; H, 7.41; N, 8.89. $C_{20}H_{22}N_2O$ requires C, 78.40; H, 7.24; N, 9.14%); $\lambda_{max}(C_6H_6)$/nm 359 (log ε 2.01); ν_{max}(KBr)/cm^{-1} 3060, 2970, 2940, 1680, 1660, 1460; $\delta_H(CDCl_3)$ 0.35 (3 H, s, *endo*-CH_3), 1.02 (3 H, s, *exo*-CH_3), 1.56 (6 H, m, CH_2), 3.41 (2 H, m_c, 4a-H and 7a-H), 6.51 (1 H, dd, ^3J 3.2, ^3J 1.8, 4′-H), 6.73 (1 H, dd, ^3J 3.2, ^4J 0.8, 3′-H), 7.40 (3 H, m, Ph), 7.53 (1 H, dd, ^3J 1.8, ^4J 0.8, 5′-H), 7.73 (2 H, dt, ^3J 6.3, ^4J 1.7, *ortho*-H_{phenyl}); $\delta_C(CDCl_3)$ 17.2 (q), 18.0 (q), 25.3 (t), 25.8 (t), 28.4 (t), 48.5 (d), 48.6 (d), 65.7 (s), 95.4 (s), 97.3 (s), 108.8 (d), 110.3 (d), 127.4 (2 × d), 127.7 (d), 128.3 (2 × d), 135.8 (s), 142.7 (d), 151.4 (s).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(3′-pyridyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1g). Colourless needles (159 mg, 99%), mp 88–89 °C (decomp.) (Found: C, 79.87; H, 7.64; N, 13.33. $C_{21}H_{23}N_3$ requires C, 79.46; H, 7.30; N, 13.24%); $\lambda_{max}(C_6H_6)$/nm 363 (log ε 2.00); ν_{max}(KBr)/cm^{-1} 2940, 2820, 1480, 1460, 1400; $\delta_H(CDCl_3)$ 0.18 (3 H, s, *endo*-CH_3), 1.00 (3 H, s, *exo*-CH_3), 1.55 (6 H, m_c, CH_2), 3.54 (2 H, m_c, 4a-H and 7a-H), 7.40–7.54 (4 H, m, arom. H), 7.72–7.77 (2 H, m, *ortho*-H_{phenyl}), 8.15 (1 H, ddd, ^3J 8.0, ^4J 2.3, ^4J 1.7, 4′-H), 8.67 (1 H, dd, ^3J 4.8, ^4J 1.4, 6′-H), 8.96 (1 H, d, ^4J 1.5, 2′-H); $\delta_C(CDCl_3)$ 16.9 (q), 17.7 (q), 25.39 (t), 25.41 (t), 28.5 (t), 48.8 (2 × d), 66.4 (s), 96.6 (s), 98.7 (s), 123.4 (d), 127.4 (2 × d), 127.9 (d), 128.4 (2 × d), 132.0 (s), 135.4 (d), 135.7 (s), 148.5 (d), 149.2 (d).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(2′-pyridyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1i). Colourless needles (159 mg, 99%), mp 100–101 °C (decomp.) (Found: C, 79.91; H, 7.72; N, 13.38. $C_{21}H_{23}N_3$ requires C, 79.46; H, 7.30; N, 13.24%); $\lambda_{max}(C_6H_6)$/nm 362 (log ε 2.01); ν_{max}(KBr)/cm^{-1} 2930, 2840, 1460, 1420, 1360; $\delta_H(CDCl_3)$ 0.19 (3 H, s, *endo*-CH_3), 1.11 (3 H, s, *exo*-CH_3), 1.56 (6 H, m, CH_2), 3.57 (1 H, m_c, 4a-H), 3.84 (1 H, m_c, 7a-H), 7.26–7.50 (4 H, m, arom. H), 7.74–7.90 (3 H, m, Ph), 8.14 (1 H, dt, ^3J 7.9, ^4J 1.1, 3′-H), 8.70 (1 H, ddd, ^3J 4.9, ^4J 1.9, ^5J 0.9, 6′-H); $\delta_C(CDCl_3)$ 16.9 (q), 18.2 (q), 25.5 (2 × t), 28.5 (t), 48.9 (d), 49.0 (d), 66.7 (s), 98.8 (s), 99.5 (s), 122.5 (d), 123.6 (d), 127.6 (2 × d), 127.7 (d), 128.3 (2 × d), 136.0 (s), 136.2 (d), 149.3 (d), 156.8 (s).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(4′-pyridyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1k). Colourless powder (159 mg, 99%), mp 142–143 °C (decomp.) (Found: C, 79.55; H, 7.28; N, 13.55. $C_{21}H_{23}N_3$ requires C, 79.46; H, 7.30; N, 13.24%); $\lambda_{max}(C_6H_6)$/nm 365 (log ε 1.99); ν_{max}(KBr)/cm^{-1} 2920, 2880, 1580, 1450, 1430; $\delta_H(CDCl_3)$ 0.17 (3 H, s, *endo*-CH_3), 1.02 (3 H, s, *exo*-CH_3), 1.52 (6 H, m_c, CH_2), 3.52 (2 H, m_c, 4a-H and 7a-H), 7.43–7.54 (3 H, m, Ph), 7.68–7.76 (4 H, m, arom. H), 8.73 (2 H, d, ^3J 5.4, 2′-H); $\delta_C(CDCl_3)$ 16.8 (q), 17.8 (q), 25.4 (2 × t), 28.5 (t), 48.8 (d), 49.0 (d), 66.5 (s), 97.0 (s), 99.0 (s), 122.4 (2 × d), 127.5 (2 × d), 127.9 (d), 128.4 (2 × d), 135.4 (s), 145.2 (s), 150.0 (2 × d).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(3′-thienyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1l). Colourless needles (143 mg, 88%), mp 116–117 °C (decomp.) (Found: C, 74.44; H, 7.15; N, 8.44; S, 9.73. $C_{20}H_{22}N_2S$ requires C, 74.49; H, 6.87; N, 8.69; S, 9.94%); $\lambda_{max}(C_6H_6)$/nm 362 (log ε 2.08); ν_{max}(KBr)/cm^{-1} 3100, 2960, 2925, 1480, 1460, 1405; $\delta_H(CDCl_3)$ 0.23 (3 H, s, *endo*-CH_3), 1.00 (3 H, s, *exo*-CH_3), 1.56 (6 H, m, CH_2), 3.35 (1 H, dt, ^3J 8.7, ^3J 7.6, ^3J 4.6, 7a-H), 3.50 (1 H, m_c, 4a-H), 7.35 (1 H, dd, ^3J 5.0, ^4J 1.3, 4′-H), 7.45 (4 H, m, 4 H, 5′-H and Ph), 7.66 (1 H, dd, ^4J 2.9, ^4J 1.3, 2′-H), 7.75 (2 H, dt, ^3J 6.7, ^4J 1.3, *ortho*-H_{phenyl}); $\delta_C(CDCl_3)$ 17.1 (q), 17.9 (q), 25.5 (t), 25.6 (t), 28.5 (t), 48.7 (d), 50.3 (d), 65.8 (s), 96.9 (s), 97.6 (s), 122.8 (d), 125.5 (d), 126.8 (d), 127.5 (2 × d), 127.7 (d), 128.3 (2 × d), 136.1 (s), 137.6 (s).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(3-furyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1m). Colourless needles (125 mg, 82%), mp 98–99 °C (decomp.)

(Found: C, 78.23; H, 7.30; N, 8.85. $C_{20}H_{22}N_2O$ requires C, 78.40; H, 7.24; N, 9.14%); $\lambda_{max}(C_6H_6)$/nm 361 (log ε 2.52); ν_{max}(KBr)/cm^{-1} 3060, 3020, 2970, 1570, 1470, 1440; $\delta_H(CDCl_3)$ 0.26 (3 H, s, *endo*-CH_3), 0.97 (3 H, s, *exo*-CH_3), 1.44 (6 H, m, CH_2), 3.15 (1 H, m, 7a-H), 3.45 (1 H, m, 4a-H), 6.62 (1 H, m, 4′-H), 7.45–7.54 (4 H, m, 5′-H and Ph), 7.74 (2 H, m, *ortho*-H_{phenyl}), 7.81 (1 H, m, 2′-H); $\delta_C(CDCl_3)$ 17.0 (q), 17.8 (q), 25.5 (t), 25.6 (t), 28.7 (t), 48.6 (d), 49.8 (d), 65.2 (s), 94.0 (s), 97.3 (s), 109.6 (d), 121.1 (s), 127.4 (2 × d), 127.7 (d), 128.3 (2 × d), 136.1 (s), 140.6 (d), 143.2 (d).

Preparation of the azoalkanes 1d–e and h

To a solution of the azoalkanes **1g**,**i** or **k** (15.6 mg, 50.0 μmol) in dry diethyl ether (20 cm^3) were added 7.17 mg (50.0 μmol) of 70% perchloric acid and the mixture stirred for 15 min at *ca.* 20 °C. The precipitate was then collected by filtration and washed twice with cold diethyl ether (10 cm^3).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(pyridinium-4-yl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine perchlorate (1d). Pale-yellow powder (20.0 mg, 96%), mp 110–111 °C (decomp.) (Found: C, 60.31; H, 6.16; N, 10.08. $C_{21}H_{24}ClN_3O_4$ requires C, 60.36; H, 5.79; N, 10.06%); $\lambda_{max}(C_6H_6)$/nm 364 (log ε 2.00); ν_{max}(KBr)/cm^{-1} 3200, 3100, 2910, 1480, 1100, 1040; $\delta_H(CD_3CN)$ 0.12 (3 H, s, *endo*-CH_3), 1.04 (3 H, s, *exo*-CH_3), 1.49 (6 H, m_c, CH_2), 3.71 (2 H, m_c, 4a-H and 7a-H), 7.45–7.58 (3 H, m, Ph), 7.72–7.78 (2 H, m, *ortho*-H_{phenyl}), 8.43 (2 H, d, ^3J 6.9, 3′-H), 8.80 (2 H, br s, 2′-H), 9.24 (1 H, br s, NH); $\delta_C(CD_3CN)$ 17.0 (q), 18.0 (q), 25.8 (2 × t), 29.3 (t), 49.8 (d), 50.6 (d), 69.1 (s), 97.7 (s), 101.2 (s), 127.1 (2 × d), 128.7 (2 × d), 129.3 (2 × d), 129.5 (2 × d), 135.9 (s), 142.5 (s, 2 × d).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(pyridinium-2-yl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine perchlorate (1e). Pale-yellow powder (20.0 mg, 96%), mp 104–105 °C (decomp.) (Found: C, 60.33; H, 6.22; N, 9.88. $C_{21}H_{24}ClN_3O_4$ requires C, 60.36; H, 5.79; N, 10.06%); $\lambda_{max}(C_6H_6)$/nm 363 (log ε 1.99); ν_{max}(KBr)/cm^{-1} 3200, 3040, 3020, 2920, 2820, 1580, 1500, 1450, 1080; $\delta_H(CD_3CN)$ 0.19 (3 H, s, *endo*-CH_3), 1.12 (3 H, s, *exo*-CH_3), 1.52 (6 H, m_c, CH_2), 3.74 (2 H, m_c, 4a-H and 7a-H), 7.46–7.59 (3 H, m, Ph), 7.76 (2 H, dd, ^3J 6.6, ^4J 1.7, 2″-H), 8.03 (1 H, t, ^3J 7.9, ^3J 5.0, 5′-H), 8.23 (1 H, d, ^3J 7.9, 3′-H), 8.59 (1 H, t, ^3J 7.5, ^4J 2.0, 4′-H), 8.87 (1 H, dd, ^3J 5.0, ^4J 1.0, 6′-H), 9.22 (1 H, br s, NH); $\delta_C(CD_3CN)$ 17.0 (q), 18.1 (q), 25.8 (t), 25.9 (t), 29.1 (t), 49.7 (d), 51.0 (d), 69.4 (s), 97.0 (s), 101.7 (s), 126.7 (d), 127.4 (d), 128.7 (2 × d), 129.4 (d), 129.6 (2 × d), 135.5 (s), 144.5 (d), 147.5 (d), 152.6 (s).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(pyridinium-3-yl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine perchlorate (1h). Colourless powder (19.6 mg, 94%), mp 98–99 °C (decomp.) (Found: C, 60.19; H, 6.09; N, 9.88. $C_{21}H_{24}ClN_3O_4$ requires C, 60.36; H, 5.79; N, 10.06%); $\lambda_{max}(C_6H_6)$/nm 363 (log ε 1.99); ν_{max}(KBr)/cm^{-1} 3200, 3020, 2920, 2880, 1440, 1080, 1010; $\delta_H(CD_3CN)$ 0.14 (3 H, s, *endo*-CH_3), 1.01 (3 H, s, *exo*-CH_3), 1.46 (6 H, m_c, CH_2), 3.68 (2 H, m_c, 4a-H and 7a-H), 7.45–7.58 (3 H, m, Ph), 7.77 (2 H, dt, ^3J 6.6, ^4J 1.7, ^5J 1.7, 2″-H), 8.10 (1 H, ddd, ^3J 8.1, ^4J 5.8, ^4J 0.7, 5′-H), 8.81 (2 H, m, arom. H), 9.13 (2 H, d, ^4J 2.0, 2′-H and NH); $\delta_C(CD_3CN)$ 17.0 (q), 17.8 (q), 25.8 (t), 25.9 (t), 29.2 (t), 49.6 (d), 50.0 (d), 68.0 (s), 96.5 (s), 100.6 (s), 128.3 (d), 128.6 (2 × d), 129.2 (d), 129.5 (2 × d), 136.2 (s), 137.8 (s), 142.2 (d), 143.0 (d), 145.7 (d).

Preparation of the azoalkanes 1a and j

To a solution of the azoalkanes **1g** or **k** (31.2 mg, 100 μmol) in dry methylene chloride (20 cm^3) were added 6.83 mg (110 μmol) of dimethyldioxirane as acetone solution[10] and stirred for 1 h at *ca.* 20 °C. Removal of the solvent at water aspirator pressure (*ca.* 20 °C/15 Torr) afforded the pure derivatives **1a** and **j**.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(*N*-oxidopyridinium-4-yl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine (1a). Colourless powder (33.1 mg, 99%), mp 58–59 °C (decomp.) (Found: C, 75.47; H, 7.26; N, 12.79. $C_{21}H_{23}N_3O$ requires C, 75.65; H, 6.95; N, 12.60%); $\lambda_{max}(C_6H_6)$/nm 362 (log ε 1.89); ν_{max}(BKr)/cm^{-1} 3000, 2920, 1460, 1460, 1280, 1230 (N–O); $\delta_H(CDCl_3)$ 0.18 (3 H, s, *endo*-CH_3), 1.01 (3 H, s, *exo*-CH_3), 1.46 (6 H, m_c, CH_2), 3.40 (1 H, m, 7a-H), 3.48 (1 H, m, 4a-H), 7.27–7.54 (3 H, m, Ph), 7.67–7.74 (4 H, m, 3′-H, *ortho*-H_{phenyl}), 8.33 (2 H, dd, ^3J 5.2, ^4J 2.0, 2′-H); $\delta_C(CDCl_3)$ 16.8 (q), 17.8 (q), 25.3 (2 × t), 28.5 (t), 48.9 (d), 49.4 (d), 66.7 (s), 96.3 (s), 99.1 (s), 124.9 (2 × d), 127.4 (2 × d), 128.1 (s), 128.5 (2 × d), 135.4 (s), 136.4 (s), 139.2 (2 × d).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(*N*-oxidopyridinium-3-yl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine (1j). Colourless powder (32.8 mg, 97%), mp 132–133 °C (decomp.) (Found: C, 75.31; H, 7.27; N, 12.87. $C_{21}H_{23}N_3O$ requires C, 75.65; H, 6.95; N, 12.60%); $\lambda_{max}(C_6H_6)$/nm 361 (log ε 1.38); ν_{max}(KBr)/cm^{-1} 3020, 2920, 1570, 1460, 1280 (N–O), 1200; $\delta_H(CDCl_3)$ 0.19 (3 H, s, *endo*-CH_3), 1.03 (3 H, s, *exo*-CH_3), 1.54 (6 H, m_c, CH_2), 3.34 (1 H, dt, ^3J 8.7, ^3J 6.2, 7a-H), 3.55 (1 H, dt, ^3J 8.9, ^3J 6.2, 4a-H), 7.41–7.51 (4 H, m, Ph), 7.70 (2 H, dt, ^3J 6.2, ^4J 2.0, *ortho*-H_{phenyl}), 7.79 (1 H, ddd, ^3J 8.0, ^4J 1.6, ^5J 1.1, 4′-H), 8.27 (1 H, ddd, ^3J 6.4, ^4J 1.7, ^5J 1.0, 6′-H), 8.62 (1 H, t, ^4J 1.4, ^5J 1.1, 2′-H); $\delta_C(CDCl_3)$ 16.8 (q), 17.8 (q), 25.3 (2 × t), 28.5 (t), 48.7 (d), 49.4 (d), 66.6 (s), 95.3 (s), 99.1 (s), 125.6 (d), 125.7 (d), 127.4 (2 × d), 128.1 (d), 128.5 (2 × d), 135.0 (s), 136.6 (s), 138.1 (d), 138.4 (d).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(4-pyridyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine-1-oxide (5i) and (1α,4α,4aα,7aα)-4,4a,5,6,7,7a-hexahydro-8,8-dimethyl-1-(4-pyridyl)-4-phenyl-1,4-methano-1*H*-cyclopenta-[*d*]pyridazine-4-oxide (5i′). To a solution of the azoalkane **1i** (31.2 mg, 100 μmol) in dry methylene chloride (20 cm^3) were added 6.83 mg (110 μmol) of dimethyldioxirane as acetone solution[10] and stirred for 18 h at *ca.* 20 °C. Removal of the solvent at water aspirator pressure (*ca.* 20 °C/Torr) afforded the azoxy derivatives **5i**/**5i**′ as a colourless powder (33.1 mg, 99%), mp 134–135 °C (decomp.) (Found: C, 75.51; H, 7.11; N, 12.74. $C_{21}H_{23}N_3O$ requires C, 75.65; H, 6.95; N, 12.60%); $\lambda_{max}(C_6H_6)$/nm 362 (log ε 1.89); ν_{max}(KBr)/cm^{-1} 3040, 2940, 1560, 1550, 1490 (N–O), 1460, 1420; δ_H of **5i** ($CDCl_3$) 0.67 (3 H, s, *endo*-CH_3), 1.05 (3 H, s, *exo*-CH_3), 1.70 (6 H, m_c, CH_2), 3.72 (1 H, dt, ^3J 8.6, ^3J 6.1, 4a-H), 4.28 (1 H, dt, ^3J 8.6, ^3J 4.9, 7a-H), 7.26–7.86 (8 H, m, 8 H, arom. H), 8.66 (1 H, dt, ^3J 5.2, ^4J 2.0, 6′-H), δ_C of **5i** ($CDCl_3$) 17.9 (q), 18.2 (q), 25.6 (t), 26.4 (t), 28.0 (t), 47.1 (d), 48.5 (d), 65.8 (s), 83.3 (s), 102.6 (s), 123.4 (d), 125.7 (2 × d), 127.5 (d), 127.9 (d), 128.0 (2 × d), 134.9 (s), 135.6 (d), 148.8 (d), 150.4 (s); δ_H of **5i**′ ($CDCl_3$) 0.71 (3 H, s, *endo*-CH_3), 1.12 (3 H, s, *exo*-CH_3), 1.69 (6 H, m_c, CH_2), 3.89 (1 H, m_c, 4a-H), 4.03 (1 H, m_c, 7a-H), 7.26–7.86 (8 H, m, arom. H), 8.67 (1 H, dt, ^3J 5.0, ^4J 1.8, 6′-H); δ_C of **5i**′ ($CDCl_3$) 17.9 (q), 18.7 (q), 25.5 (t), 26.2 (t), 28.0 (t), 47.0 (d), 48.9 (d), 66.0 (s), 83.5 (s), 102.8 (s), 122.4 (d), 123.3 (d), 128.3 (2 × d), 128.9 (d), 129.3 (2 × d), 129.6 (s), 136.3 (d), 149.1 (d), 155.9 (s).

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