The EPR *D* parameter as a measure of spin delocalization in cyclopentane-1,3-diyl triplet diradicals with extended conjugation π-type substituents

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π-Substituted cyclopentane-1,3-diyl triplet diradicals **2** were readily prepared from the corresponding azoalkanes **1** by photodenitrogenation in a 2-methyltetrahydrofuran matrix at 77 K. The *D* values of these triplet diradicals, obtained from the EPR spectra under matrix isolation, depend on the π substituent in the order butadienyl > 2-anthryl > vinyl > 2-naphthyl > phenyl. Good linear correlations of the *D* values have been obtained with the reported hyperfine coupling constants (α-hfc), with the *ab initio* (B3LYP) spin densities for the corresponding monoradicals **3**, and with the radical stabilization energies (RSE). The present results for these extended π systems are compared with those for previously reported heteroaryl-substituted triplet diradicals.

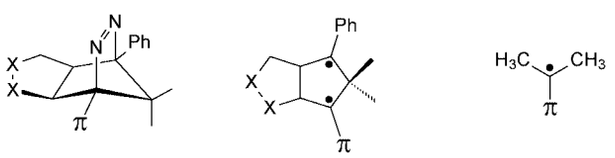
Introduction

The zero-field splitting parameters *D* of localized 1,3-disubstituted triplet diradicals **2**, which are accurately determined by EPR spectroscopy under matrix isolation [2-methyltetrahydrofuran (MTHF), 77 K], provide important information on the electronic properties of such high-spin systems.[1] The *D* value, which lies between 0.03 and 0.05 cm^{-1} for these triplet species, derives from the dipole–dipole interaction between the two unpaired spins and reflects the electronic nature of the diradical. It depends on the spin densities ρ_B and ρ_A at the two radical sites and the distance d_{AB} between the two radical centers, which for the cyclopentanediyl triplet diradicals **2** is *ca.* 238 pm (eqn. 1).[2] The spin densities ρ_B and ρ_A vary with

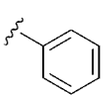
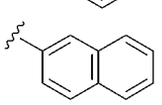
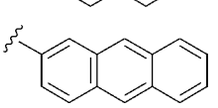
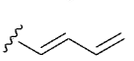
$$D = \frac{3\mu_0 g^2 \mu_B^2}{16\pi}\left(\frac{\rho_A \rho_B}{d_{AB}^3}\right) \qquad (1)$$

the spin-delocalizing properties of the π substituents, so that the change of the *D* parameter of the triplet diradicals **2** reflects the nature and efficacy of the substituents to interact with the radical center. For the so-far investigated aryl substituents[1,3] (phenyl groups with a large variety of substituents in the *meta* and *para* positions), only relatively weak but measurable electronic effects were observed.

Herein we have examined the effect of the spin-delocalizing ability of extended π systems on the *D* parameter. The triplet diradicals **2** necessary for this investigation were readily prepared from the azoalkanes **1** by photodenitrogenation in a MTHF matrix at 77 K. The present results for these extended π systems have been compared with those for previously reported[3] heteroaryl-substituted triplet diradicals.



1 **2** **3**

	X—X	π
a	CH_2—CH_2	
b	CH_2—CH_2	
c	CH=CH	
d	CH_2—CH_2	
e	CH_2—CH_2	

Results

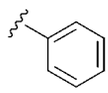
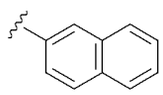
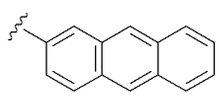
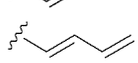
Synthesis

The aryl-substituted azoalkanes **1a**, **1b** and **1c** were prepared according to the Hünig route, in analogy to reported procedures.[4] To avoid regioisomers, the unsaturated azoalkanes were transformed into the saturated ones **1**, with the exception of the anthryl derivative **1c**. In the case of **1c**, attempts to hydrogenate catalytically the cyclopentenyl double bond also reduced the anthryl substituent to 9,10-dihydroanthracene; reoxidation of the latter led to a complex product mixture. For this reason, the unsaturated derivative **1c** was directly used to determine the *D* parameter, but the effect of cyclopentenyl *versus* cyclopentanyl annelation on the *D* parameter is negligible. The azoalkanes **1d** and **1e** with olefinic substituents were made by Wittig reaction of the known azoalkane **1f** with the corresponding phosphoranes, as displayed in Scheme 1.[5,6]

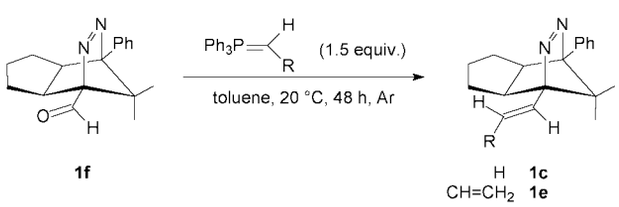
EPR Spectroscopy

Photolysis of the azoalkanes **1** in a 2-methyltetrahydrofuran glass matrix at 77 K with the 364 nm line of an argon-ion laser afforded the persistent triplet diradicals **2**. Through analysis of

Table 1 Experimental *D* values of the triplet diradicals **2** and theoretical α spin densities of the corresponding monoradicals **3**

Compound **2**, **3**	π	|*D*/*hc*|[a] (**2**)	ρ_α[b] (**3**)	α-hfc[c] (**3**)
a		0.0506	0.742	16.25
b		0.0485	0.693	n.a.[d]
c		0.0436[e]	0.589	n.a.[a]
d		0.0473	0.686	14.37
e		0.0333	0.394	10.16

[a] Given in cm^{-1} for the triplet diradicals **2**, measured at 77 K in a 2-MTHF matrix, error ±0.0002 cm^{-1}, $|E/hc| < 0.002\ cm^{-1}$. [b] B3LYP/6-31G*-calculated spin densities of the α-carbon atom in the radical **3**. [c] EPR α-hyperfine coupling constant (α-hfc) in G. [d] Not available. [e] Determined for the unsaturated derivative **2c**.



Scheme 1

the Z signals in the EPR spectra (for a typical one *cf*. Fig. 6 in ref. 1), the *D* values were determined as half of the distance between the low- and the high-field signals; the *E* values are small (≤0.002 cm^{-1}). The EPR data are summarized in Table 1. The experimental *D* values in Table 1 have been arranged in descending order, with the phenyl derivative **2a** as the highest (0.0506 cm^{-1}) and butadienyl **2e** as the lowest (0.0333 cm^{-1}). Compared to the parent system **2a**, all triplet diradicals **2** possess lower *D* values; this implies that the spin density at the radical center is lower compared to the phenyl-substituted triplet diradical and, hence, the spin is better delocalized by the π substituent. The electronic substituent effect on the spin delocalization will now be discussed and compared in terms of heteroaryl substitution, *e.g*. thiophene, furan and pyridine.[3]

Discussion

In all of the triplet diradicals **2** one radical site is kept constant (phenyl substitution) and, thus, the experimentally assessed changes in the *D* parameter must derive from the different π substituents. Comparison of the reported α-hyperfine coupling constants[7] (α-hfc) of the corresponding monoradicals **3** (2-naphthyl and 2-anthryl cases are not known) with the *D* parameter of the triplet diradicals **2** reveals a good linear correlation (Fig. 1, $r^2 = 0.959$, $n = 8$). This manifests that the two EPR-spectral quantities (|*D*/*hc*| and α-hfc) reflect reliably the spin-delocalizing ability of the π substituent, *i.e*. the more effective the delocalization the lower is the *D* value of the triplet diradical **2** and the α-hfc value of the corresponding monoradical **3**. Hence, the spin-delocalizing ability of the π substituents follows the order butadienyl > 2-furyl > 2-thienyl > vinyl > *m*-pyridyl > phenyl > *p*-pyridyl > 3-thienyl.

Since both EPR parameters are linearly proportional to the spin density (*ρ*) at the radical site [*cf*. eqn. (1) and McConnel equation (ref. 6)], this implies that the unpaired electron is more delocalized by the π substituent and, consequently, the *ρ* value is lower. This correspondence is convincingly demonstrated

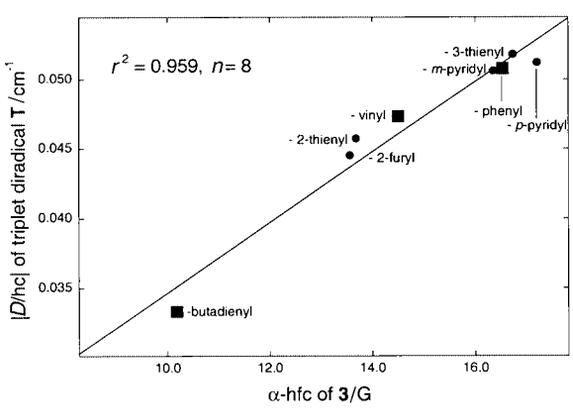


Fig. 1 EPR-spectral *D* parameter of the triplet diradicals **2** *versus* α-hyperfine coupling constants of the corresponding monoradicals **3** (*D* values of Table 1 marked by filled squares).

in Fig. 2, in which the computed (*ab initio* B3LYP/6-31G* method[8]) spin densities of the monoradical fragments **3** linearly correlate ($r^2 = 0.982$, $n = 13$) with the experimental *D* parameter of the triplet diradicals **2** (denoted with filled squares).†

It has been reported for benzyl- and cumyl-type radicals that the α spin density constitutes a useful probe to determine radical stabilization energies (RSE). We have shown previously that the *D* parameter of the triplet diradicals **2** correlates well with the α spin density of the corresponding monoradical **3** (Fig. 2).[1] Consequently, it was of interest to assess whether the variations in the experimental *D* parameter of the triplet diradicals **2** caused by the present extended conjugation π substituents correlates with the radical stabilization energy computed from the corresponding monoradical **3**. Despite all the work on radical stabilization,[9] it is surprising that extended π systems, in particular the phenyl, naphthyl and anthryl set, have not been evaluated so far and correlated with an experimental parameter. Presumably such aryl π-type radicals **3a**–**c** are not readily accessible and their delocalization propensity assessed by experimental means. This clearly accentuates the advantage of the conveniently prepared localized triplet diradicals **2** and their experimentally accurately determinable *D* parameters.

† A reviewer has called our attention to the fact that the simple HMO spin densities for the radicals in Table 1 give a good correlation ($r^2 = 0.981$, $n = 5$). Although we were aware of this good correspondence, in Fig. 2 are also included the heteroaryl cases, for which a higher lever of theory (B3LYP/6-31G*) is necessary.

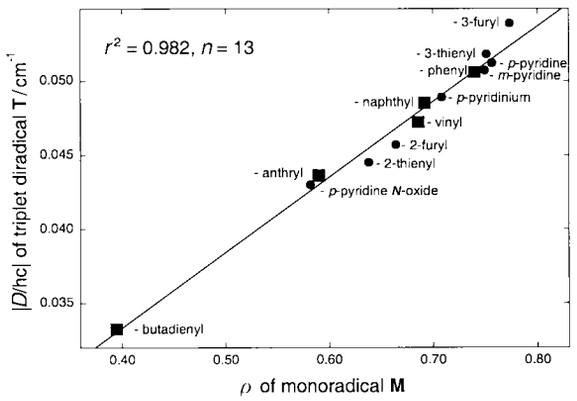


Fig. 2 Experimental D parameter (cm^{-1}) of the triplet diradicals **2** *versus* B3LYP-calculated α spin density of the corresponding monoradicals **3** (D values of Table 1 denoted by filled squares).

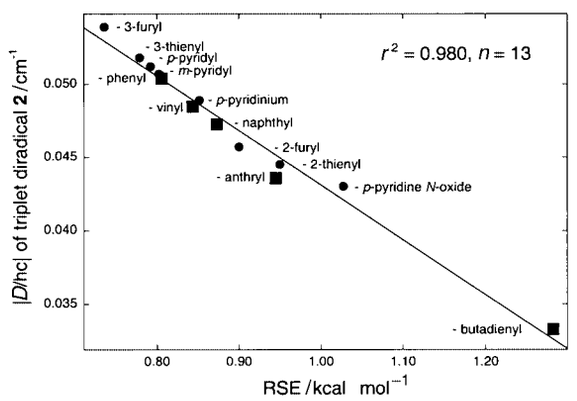


Fig. 3 EPR-spectral D parameter of the triplet diradicals **2** *versus* radical stabilization energies of the corresponding monoradicals **3** (D values of Table 1 denoted by filled squares).

RSE values may be conveniently computed from the difference between the energy of the 90° (no delocalization) and the 0° (maximum delocalization) conformers.[1,10] These computations were performed by using the PM3 (AUHF) method, implemented in the Vamp 6.1 program package. The excellent correlation ($r^2 = 0.980$, $n = 13$) between the calculated RSE values for the monoradicals **3** with the experimental D values of the triplet diradicals **2** (Fig. 3) unmistakingly establishes that the D parameter provides a quantitative measure of the electronic factors responsible for the radical stabilization in such π-type radicals, which includes aryl, heteroaryl and olefinic substituents. Thus, we may employ directly the D value to assess radical-stabilizing effects of π radicals through delocalization, as illustrated for the cases studied herein.

Compared to the phenyl[2] system **2a** (0.0506 cm^{-1}), only the 3-furyl (0.0539 cm^{-1}) and 3-thienyl (0.0518 cm^{-1}) groups have a lower radical-stabilizing ability, while all the other π substituents have lower D values and, therefore, possess a better radical-delocalizing propensity. The 3-furyl and 3-thienyl derivatives are cross-conjugated π systems compared to the remaining extended conjugation ones, which accounts for the more effective radical stabilization of the latter cases. Thus, for the three aryl-substituted triplet diradicals with phenyl **2a** (0.0506 cm^{-1}), 2-naphthyl **2b** (0.0485 cm^{-1}) and 2-anthryl **2c** (0.0436 cm^{-1}) groups, the radical stabilization increases in this order in view of better delocalization as the π system becomes larger. However, only the 2-anthryl derivative **2c** is a better delocalizer than the vinyl one **2d**, but worse compared to the butadienyl **2e**, which clearly indicates that aryl π systems are less effective in stabilizing radical sites than are olefinic ones; thus, the delocalizing power follows the order phenyl (**2a**) < 2-naphthyl (**2b**) < vinyl (**2d**) < 2-anthryl (**2c**) < butadienyl (**2e**).

Our present data on the D parameter for a variety of π-substituted triplet diradicals **2** and the spin densities for the corresponding monoradicals **3** have allowed us to probe experimentally and theoretically the electronic effects of extended conjugation on radical stabilization. The ease of preparing the required azoalkanes **1** as precursors for the generation of the matrix-isolated triplet diradicals **2** through photodeazetation and the accuracy and convenience of measuring the D parameter by EPR spectroscopy offer definite advantages to assess electronic effects in monoradicals.

Experimental

General aspects

The NMR spectra were recorded on a Bruker AC200 or AC250 instrument with $CDCl_3$ as the solvent and internal standard. J Values are given in Hz. The infrared spectra were measured on a Perkin-Elmer Infrared Ratio Recording Spectrometer 1420 and the UV spectra on a Hitachi U 3200 spectrometer. The melting points were taken on a Büchi SMP-535 or B-545 apparatus and the combustion analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry (University of Wuerzburg). Solvents and commercially available chemicals were purified by standard procedures or used as bought. Column chromatography was carried out on silica gel (0.032–0.063 mm, Woelm) with an adsorbent : substrate ratio of *ca.* 100 : 1. Thin layer chromatography (TLC) was performed on Polygram Sil G/UV$_{254}$ (40 × 80 mm) from Macherey & Nagel. Irradiations were carried out with the 333, 351, and 364 nm UV lines (widened beam) of a CW argon-ion laser (INNOVA 100, Coherent Co.).

Compounds **1a**, **1d** and **1f** are known and were prepared according to the methods described below or elsewhere.

1-(2′-Anthryl)-3-phenylpropane-1,3-dione. Sodium amide (100 mmol) was suspended in 200 ml of dry THF. Methyl benzoate (50 mmol) and 1-(2′-anthryl)ethanone (50 mmol) were added under cooling and the resulting mixture was stirred at *ca.* 20 °C for 16 h. The dark solution was poured onto 100 g of crushed ice and acidified with 85% H_3PO_4 (*ca.* 5 ml). The product was extracted with dichloromethane (3 × 100 ml), dried over $MgSO_4$, the solvent evaporated (*ca.* 25 °C/10 mbar) to afford the crude product, which was purified by recrystallization from ethanol to yield 10.4 g (64%) yellow plates (mp 147–148 °C). $\tilde{\nu}$ (KBr) = 2960, 2940, 1590, 1440, 1300, 1250, 1170, 1110, 1030, 840 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 7.04 (s, 1H, enol 2-H), 7.48–7.58 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.93 (m, 6H, 3′-, 4′-, 5′-, 8′-, 2″-, 6″-H), 8.44 (s, 1H, 9′-H), 8.57 (s, 1H, 10′-H), 8.73 (s, 1H, 1′-H); δ_C(63 MHz; $CDCl_3$) 93.5 (d; C-2), 122.2 (d), 125.9 (d), 126.2 (d), 126.5 (d), 126.6 (d), 127.2 (d), 127.9 (d), 128.2 (d), 128.4 (d), 128.7 (d), 128.8 (d), 129.4 (d), 130.1 (d), 130.5 (s), 132.1 (d), 132.3 (s), 132.5 (s), 132.8 (s), 133.0 (s), 135.6 (s), 185.1 (s, C-1), 185.8 (s, C-3). Calc. for $C_{23}H_{16}O_2$: C, 85.21; H, 4.97. Found: C, 84.91; H, 4.98%.

Preparation of 2,2-dimethylpropane-1,3-diones

The substituted 1,3-diaryl-2,2-dimethylpropane-1,3-diones were prepared by the literature procedure[1,4a] through dimethylation of the corresponding 1,3-diarylpropane-1,3-diones and purified by recrystallization from cyclohexane–benzene (1 : 1).

2,2-Dimethyl-1-(2′-naphthyl)-3-phenylpropane-1,3-dione. 58%, colorless needles, mp 89–90 °C; $\tilde{\nu}$ (KBr) = 2980, 2910, 1640, 1580, 1490, 1300, 1240, 1160, 1120, 980 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 1.70 (s, 6H, 2-CH_3), 7.18–7.62 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.74–7.82 (m, 2H, 2″-, 6″-H), 7.88–8.10 (m, 3H, 4′-, 5′-, 8′-H), 8.38 (s, 1H, 1′-H), 8.50 (d, ^3J = 8.7, 1H, 3′-H); δ_C(63 MHz; $CDCl_3$) 25.5 (q, 2 × 2-CH_3), 59.5 (s, C-2), 124.7 (d, C-7′), 126.7 (d, C-3′), 126.9 (d, C-6′), 127.5 (s, C-2′), 127.7 (d, C-1′), 128.2 (d, C-4′), 128.5 (d, C-3″, C-5″), 128.8 (d, C-5′),

129.1 (d, C-8′), 129.4 (d, C-2″, C-6″), 132.3 and 132.8 (2 × s, 4a′ and 8a′), 132.9 (d, C-4″), 135.2 (s, C-1″), 200.1 and 200.5 (2 × s, C-1 and C-3). Calc. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.18; H, 5.97%.

2,2-Dimethyl-1-(2′-anthryl)-3-phenylpropane-1,3-dione. 38%, colorless needles, mp 120–121 °C; $\tilde{\nu}$ (KBr) = 3060, 2860, 1660, 1500, 1410, 1310, 1260, 1060, 990, 880 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 1.70 (s, 6H, 2-CH_3), 7.26–7.50 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.87–8.03 (m, 6H, 3′-, 4′-, 5′-, 8′-, 2″-, 6″-H), 8.31 (s, 1H, 9′-H), 8.44 (s, 1H, 10′-H), 8.50 (s, 1H, 1′-H); δ_C(63 MHz; $CDCl_3$) 25.6 (q, C-2-CH_3), 59.5 (d, C-2), 123.4 (d), 125.9 (d), 126.7 (d), 128.0 (d), 128.6 (d), 128.8 (d), 129.1 (d), 129.3 (d), 129.4 (d), 130.4 (s), 130.9 (d), 131.9 (d), 132.2 (d), 132.3 (s), 132.4 (d), 132.5 (s), 132.7 (s), 132.9 (d), 133.3 (s), 135.8 (s), 199.9 and 200.6 (2 × s, C-1 and C-3). Calc. for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 84.99; H, 5.68%.

Preparation of the 3,5-diaryl-4,4-dimethylisopyrazoles

The cyclization of the 2,2-dimethyl-1,3-diones with hydrazine hydrate to the isopyrazoles was carried out according to the literature procedures.[1,4a] The products were purified by recrystallization from benzene–cyclohexane (1 : 1).

4,4-Dimethyl-3-(2′-naphthyl)-5-phenyl-4*H*-pyrazole. 69%, colorless powder, mp 150–151 °C; ν (KBr) = 2980, 2920, 1510, 1400, 1310, 1160, 1120, 1100, 1060, 850 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 1.80 (s, 6H, 4-CH_3), 7.50–7.59 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.86–7.97 (m, 3H, 4′-, 5′-, 8′-H), 8.11 (m, 2H, 2″-, 6″-H), 8.34 (dd, ^3J = 8.7, ^4J = 1.7, 1H, 3′-H), 8.41 (d, ^4J = 1.7, 1H, 1′-H); δ_C(63 MHz; $CDCl_3$) 23.2 (q, C-4-CH_3), 58.7 (s, C-4), 125.1 (d, C-7′), 126.6 (d, C-6′), 127.4 (s, C-2′), 127.6 (d, C-3′), 127.8 (d, C-2″, C-6″), 127.9 (d, C-1′), 127.9 (d, C-4′), 128.6 (d, C-3″, C-5″), 128.8 (d, C-8′), 128.9 (d, C-5′), 130.0 (s, C-1″), 130.8 (d, C-4″), 132.9 and 134.3 (2 × s, C-4a′ and C-8a′), 178.9 and 179.2 (2 × s, C-3 and C-5). Calc. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.34; H, 6.48; N, 9.31%.

3-(2′-Anthryl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole. 66%, colorless powder, mp 180–181 °C; $\tilde{\nu}$ (KBr) = 3000, 2960, 2880, 1560, 1470, 1450, 1390, 1380, 1140, 1110 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 1.82 (s, 6H, C-4-CH_3), 7.48–7.53 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.98–8.17 (m, 6H, 3′-, 4′-, 5′-, 8′-, 2″-, 6″-H), 8.39 (s, 1H, 9′-H), 8.43 (s, 1H, 10′-H), 8.53 (s, 1H, 1′-H); δ_C(63 MHz; $CDCl_3$) 23.3 (q, C-4-CH_3), 58.4 (s, C-4), 124.3 (d), 125.8 (d), 126.1 (d), 126.2 (d), 126.7 (d), 127.8 (d), 127.9 (2 × d), 128.1 (d), 128.4 (d), 128.8 (2 × d), 129.9 (d), 130.7 (s), 130.8 (d), 131.6 (s), 131.7 (s), 131.9 (s), 132.1 (s), 132.6 (s), 178.6 and 179.2 (2 × s, C-3 and C-5). Calc. for $C_{25}H_{20}N_2$: C, 86.18; H, 5.79; N, 8.04. Found: C, 85.97; H, 5.83; N, 7.94%.

Preparation of the azoalkanes

The azoalkanes were obtained by acid-catalysed cycloaddition of the isopyrazoles with cyclopentadiene under the same conditions as described in the literature.[1,4a] Analytically pure samples were obtained by silica-gel chromatography (CH_2Cl_2–ethyl acetate; 5 : 1).

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(2′-naphthyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine. 40%, colorless powder, mp 137–138 °C; $\tilde{\nu}$ (KBr) = 2900, 1430, 1340, 1300, 1260, 1250, 1150, 1110, 1070, 1030 cm^{-1}. δ_H(250 MHz; $CDCl_3$) 0.25 (s, 3H, 9-H), 1.02 (s, 3H, 10-H), 2.25 (m, 2H, 7-H), 3.72 (m, 1H, 7a-H), 4.25 (m, 1H, 4a-H), 5.54 (m, 2H, 5-, 6-H), 7.36–7.56 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.76–7.98 (m, 6H, 3′-, 4′-, 5′-, 8′-, 2″-, 6″-H), 8.34 (s, 1H, 1′-H); δ_C(63 MHz; $CDCl_3$) 17.1 (q, C-9), 17.6 (q, C-10), 31.7 (t, C-7), 43.2 (d, C-7a), 56.8 (d, C-4a), 64.4 (s, C-8), 96.9 (s, C-4), 98.0 (s, C-1), 125.5 (d, C-3′), 125.8 (d, C-7′), 126.5 (d, C-6′), 126.6 (d, C-1′), 126.8 (d, C-4′), 127.3 (d, C-6), 127.6 (d, C-2″, C-6″), 127.7 (d, C-4″), 128.1 (d, C-3″, C-5″), 128.3 (d, C-5′), 128.3 (d, C-8′), 133.7 (d, C-5), 134.0 (s, C-2′), 134.1 (s, C-4a′), 134.1 (s, C-8a′), 136.2 (s, C-1″). Calc. for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.42; H, 6.50; N, 7.58%.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-1-(2′-anthryl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine. 32%, colorless powder, mp 101–102 °C, decomp.; $\tilde{\nu}$ (KBr) = 3050, 2920, 1570, 1525, 1460, 1440, 1370, 1020, 990, 890 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 0.28 (s, 3H, 9-H), 1.11 (s, 3H, 10-H), 2.25–2.31 (m, 2H, 7-H), 3.73 (m, 1H, 7a-H), 4.19 (m, 1H, 4a-H), 5.55 (s, 2H, 5-, 6-H), 7.43–7.55 (m, 5H, 6′-, 7′-, 3″-, 4″-, 5″-H), 7.80–7.85 (m, 3H, 4′-, 2″-, 6″-H), 8.03–8.06 (m, 2H, 5′-, 8′-H), 8.13 (d, ^3J = 8.9, 1H, 3′-H), 8.49–8.55 (m, 3H, 1′-, 9′-, 10′-H); δ_C(63 MHz; $CDCl_3$) 17.2 (q, C-9), 17.6 (q, C-10), 31.8 (t, C-7), 43.3 (d, C-7a), 56.8 (d, C-4a), 64.5 (s, C-8), 97.0 (s, C-4), 98.1 (s, C-1), 124.9 (d), 125.1 (d), 125.5 (d), 126.0 (d), 126.6 (s), 126.9 (d), 127.2 (d), 127.2 (d), 127.7 (2 × d), 127.9 (d), 128.2 (2 × d), 128.3 (d), 131.4 (2 × s), 131.9 (2 × s), 133.6 (s). Calc. for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.78; H, 6.30; N, 6.60%.

Preparation of the saturated azoalkanes

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(2′-naphthyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine. The saturated azoalkane was obtained (98% yield) by hydrogenation of the unsaturated azoalkane under a hydrogen-gas atmosphere on a 10% Pd/charcoal catalyst according to the literature procedure[1,4a] as colorless needles, mp 133–134 °C, decomp.; $\tilde{\nu}$ (KBr) = 3020, 2940, 1525, 1480, 1450, 1370, 1020, 990, 890, 870 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 0.24 (s, 3H, 9-H), 1.07 (s, 3H, 10-H), 1.58–1.68 (m, 6H, 5-, 6-, 7-H), 3.59–3.69 (m, 2H, 4a-, 7a-H), 7.39–7.47 (m, 2H, 6′-, 7′-H), 7.50–7.57 (m, 3H, 3″-, 4″-, 5″-H), 7.79–7.83 (m, 2H, 2″-, 6″-H), 7.88–7.98 (m, 4H, 3′-, 4′-, 5′-, 8′-H), 8.38 (s, 1H, 1′-H); δ_C(63 MHz; $CDCl_3$) 17.0 (q, C-9), 17.9 (q, C-10), 25.5 (t, C-5), 25.5 (t, C-7), 28.5 (t, C-6), 48.9 (d, C-4a), 49.0 (d, C-4a), 66.4 (s, C-8), 98.4 (s, C-1), 98.5 (s, C-2), 125.3 (d, C-3′), 125.9 (d, C-7′), 126.0 (d, C-6′), 126.6 (d, C-1′), 127.5 (d, C-4″), 127.6 (d, C-2″, C-6″), 127.7 (d, C-4′), 127.9 (d, C-8′), 128.2 (d, C-5′), 128.3 (d, C-3″, C-5″), 132.8 (s, C-4a′), 133.2 (s, C-8a′), 133.8 (s, C-2′), 136.1 (s, C-1″). Calc. for $C_{26}H_{26}N_2$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.14; H, 7.29; N, 7.33%.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(butadienyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1e). The azoalkane **1e** was obtained by Wittig olefination[5] by stirring a mixture of the azoalkane **1f** (30.0 mmol) with triphenylpropenylidenephosphorane (45.0 mmol) in 60 ml toluene under exclusion of air at room temperature (*ca.* 20 °C) for 48 h. Extraction with diethyl ether (3 × 50 ml) and SiO_2 chromatography (10 : 1 CH_2Cl_2–ethyl acetate) gave colorless plates (48%, mp 127 °C, decomp.); $\tilde{\nu}$ (KBr) = 3030, 2930, 1580, 1540, 1460, 1440, 1330, 1020, 990, 890 cm^{-1}. δ_H(200 MHz; $CDCl_3$) 0.27 (s, 3H, 9-H), 1.03 (s, 3H, 10-H), 1.58–1.68 (m, 6H, 5-, 6-, 7-H), 3.59–3.69 (m, 2H, 4a-, 7a-H), 5.50 (d, ^2J = 26.0, ^3J = 11.8, 2H, CH=CH_2), 5.86 (d, ^3J = 11.6, 1H, C*H*=CH–CH), 6.42 (dd, ^3J = 11.3, ^3J = 11.6, 1H, C*H*–CH=CH_2), 6.47 (dd, ^3J = 11.3, ^3J = 11.8, 1H, CH–C*H*=CH_2), 7.15–7.24 (m, 2H, *m*-Ph), 7.31–7.39 (m, 3H, *o, p*-Ph); δ_C(63 MHz; $CDCl_3$) 17.0 (q, C-9), 17.9 (q, C-10), 25.5 (t, C-5), 25.5 (t, C-7), 28.5 (t, C-6), 48.9 (d, C-4a), 49.0 (d, C-7a), 66.4 (s, C-8), 98.4 (s, C-1), 99.3 (s, C-4), 114.2 (t, CH–CH=*C*H_2), 121.7 (d, *C*H=CH–CH), 125.3 (d, CH–*C*H=CH_2), 127.3 (2 × d, *m*-Ph), 128.3 (d, *p*-Ph), 129.6 (2 × d, *o*-Ph),133.8 (d, *C*H–CH=CH_2), 135.5 (s, *ipso*-Ph). Calc. for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.51; H, 8.29; N, 9.43%.

EPR Spectroscopy

A sample of the azoalkane **1** (*ca*. 5 μmol) in 2-methyltetrahydrofuran (*ca*. 0.5 ml) was placed into the EPR sample tube, deaerated by purging with a slow stream of argon gas for *ca*. 10 min and sealed. The glass matrix was formed by cooling the sample to 77 K in liquid nitrogen. The triplet diradicals **2** were generated by irradiation with the 333, 351 and 364 nm lines of a INNOVA-100 CW argon-ion laser (widened beam, 2.0 W MLUV, 2 min) at 77 K. The EPR spectrum was recorded on a Bruker ESP-300 spectrometer (9.43 GHz, spectra accumulation with the Bruker 1620 data system, $n \geq 5$). The D values were determined by analysis of the Z signals.

Computations

The full geometry optimization of the monoradicals **3** was carried out on the highest symmetry with a planar arrangement of the allyl or aryl groups at the radical site. The PM3 method and AUHF wavefunction were used, which are provided in the Vamp 6.1 program package and run on an IRIS INDIGO Silicon Graphic Workstation.[11] The spin densities were determined by a single-point CI calculation. Alternatively, these values were calculated by the B3LYP/6-31G* method, which is provided in the Gaussian 98 program.[8] Both methods result in spin expectation $\langle S^2 \rangle$ values between 0.75 and 0.76.

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