The EPR *D*-parameter of 1,3-diarylcyclopentane-1,3-diyl triplet diradicals as a probe for steric substituent effects in benzyl-type radicals †

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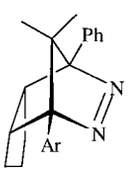
The zero-field splitting *D* parameter of a set of *ortho*-substituted 1,3-diarylcyclopentane-1,3-diyl triplet diradicals **3** has been determined by EPR spectroscopy in a 2-methyltetrahydrofuran glass matrix at 77 K. While for *meta*- and *para*-substituted triplet diradicals **3** the *D* parameter is only a function of the electronic nature (spin donor *versus* spin acceptor) of the substituent, for the *ortho*-substituted derivatives the steric influence must also be considered. We show herein that the steric effect of the *ortho* substituent diminishes delocalization of the cumyl spin density into the aromatic ring through twisting of the π system out of conjugation with the cumyl radical center; indeed, the steric effect may outweigh the electronic influence of the substituent. The computed (PM3) spin density of the minimum-energy conformer reproduces well the experimentally observed steric effect on the *D* parameter of the triplet diradicals **3**. These results demonstrate that the EPR-spectroscopic *D* parameter serves as a sensitive probe for steric as well as electronic substituent effects.

Introduction

The zero-field splitting parameter *D* of the localized 1,3-diaryl-substituted triplet diradicals **3**, which are accurately



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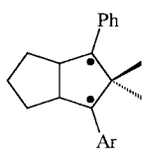
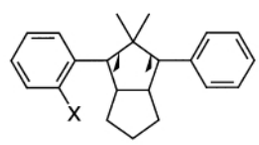
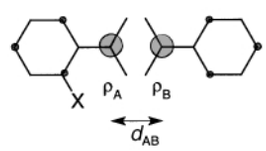


3

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 is *ca.* 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,[2] which for the cyclopentanediyl triplet diradicals **3** is *ca.* 238 pm [eqn. (1)].[3] The spin densities ρ_B and ρ_A vary with the spin-delocalizing properties of the substituted aryl groups, such that the change of the *D* parameter in the triplet diradicals **3** reflects the nature and efficacy of the substituent on the aryl group in interacting with the cumyl spin moiety. While for *meta* and *para* substituents only electronic effects operate, for *ortho* substituents additional steric effects are expected. Depending on the spin-accepting (SA) or spin-donating (SD) ability of the substituent, electronic effects either lower (SA) or raise (SD)



3a-f



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

the *D* value;[4] for the steric influence, *D* should always increase. This is due to twisting of the cumyl spin center out of conjugation with the aromatic π system, thereby hindering the delocalization of spin; in other words, the spin is more effectively localized at the cumyl site.

In this work we have examined a selected set of *ortho*-substituted triplet diradicals **3** derived from azoalkanes **1** by photodenitrogenation in MTHF matrix at 77 K to assess the efficacy of steric effects of *ortho* substitution in the triplet diradicals **3**. As displayed by the results herein, such steric effects may outweigh electronic ones.

Results

Syntheses

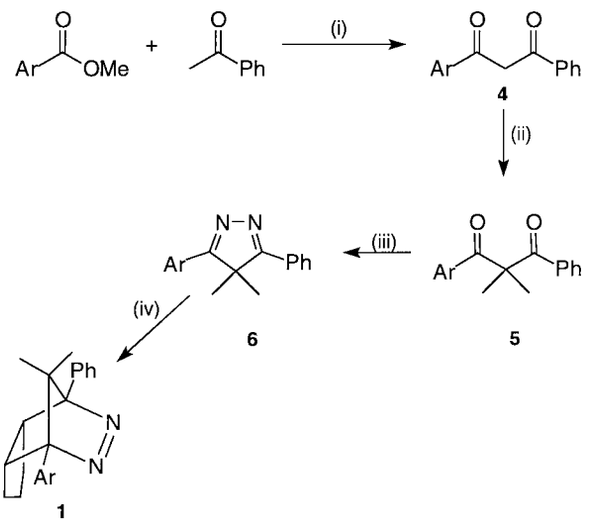
The substituted 4*H*-pyrazoles **6** were prepared in analogy to reported procedures (Scheme 1).[5] Due to the steric hindrance of the *ortho* substituents, the usual synthetic route to the azoalkanes **1** failed, namely the acid-catalyzed cycloaddition of the dienophile to the 4*H*-pyrazoles **6**. High pressure (12.5 kbar) and elevated temperature (≥ 100 °C) were necessary to force the cycloaddition with cyclopentene as the dienophile. The yields

† Computational details such as heats of formation of the diradicals **3** and the spin densities of the cumyl position of the radicals **2** as a function of the torsional angle θ are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/2723, otherwise available from BLDSC (SUPPL. NO. 57657, pp. 2) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

Table 1 *D* values and torsional angles (θ) of *ortho*-substituted diradicals **3**

Diradical	Substituent	D_{ortho} [a]	θ_A [b]	θ_B [c]	$\Delta\theta_B$ [d]	D_{para} [e]
3a	H	5.06	0	50	0	5.06
3b	F	5.14	—	51	1	5.14
3c	Cl	5.07	3	55	5	5.01
3d	Br	5.13	14	71	21	5.03
3e	CH_3	5.12	15	73	23	5.05
3f	OCH_3	[f]	—	—	—	5.08

[a] $|D/hc|\cdot10^{-2}$ in cm^{-1}, measured in a 2-MTHF matrix at 77 K, error ±0.00002 cm^{-1}; $|E/hc| < 0.002$ cm^{-1}. [b] Torsional angle calculated according to method A (see text). [c] Torsion angle calculated according to method B (see text). [d] Chance of the torsional angle θ_B relative to the parent system **3a**. [e] Ref. 4*b*. [f] No EPR signal detected.



Scheme 1 Synthesis of azoalkanes **1**. (i) $NaNH_2$, THF, *ca.* 20 °C, 1–2 d; (ii) K_2CO_3, $(n\text{-Bu})_4NBr$, toluene, *ca.* 80 °C, 2 d; (iii) $N_2H_4\cdot H_2O$, $CHCl_3$, 60 °C, 1 d; (iv) cyclopentene, toluene, 110 °C, 12.5 kbar, 2 d.

of the azoalkanes **1** were low because at *ca.* 100 °C much denitrogenation to the corresponding housane took place, while at *ca.* 80 °C no cycloaddition occurred.

EPR Spectroscopy

Except for the derivative **1f**, the photolysis of the azoalkanes **1** in 2-methyltetrahydrofuran (MTHF) glass at 77 K with the 364-nm line of an argon-ion laser led to the persistent triplet diradicals **3**. For the *ortho*-methoxy-substituted case no EPR signal was observed. Analysis of the Z signals in the EPR spectra (for a typical one, *cf.* Fig. 1 in ref. 6) afforded the *D* parameter as one-half of the distance between the low- and the high-field peaks; the *E* parameters were expectedly very small (≤0.002 cm^{-1}).

The EPR data are summarized in Table 1. As can be seen, all *ortho*-substituted triplet diradicals **3** possess higher *D* values compared to the parent system **3a**. This implies that a higher spin density is located at the cumyl position for the *ortho*-substituted than for the parent triplet diradical and, hence, there is less delocalization of spin into the aromatic ring. The highest *D* value (0.0514) was obtained for the fluoro substituent in **3b** and the lowest one (0.0507) for the chloro substituent in **3c**.

Determination of the torsional angle

The efficacy of spin delocalization by the aryl groups from the cumyl position in the triplet diradicals **3** depends on the torsional angle (θ) about the C–C bond that connects the two structural units, as displayed in Fig. 1 for the parent system **2a**. The spin densities of the cumyl-radical fragments were calculated by the PM3-AUHF/CI semiempirical method [7,8] as a function of the θ angle. For the coplanar conformation ($\theta = 0°$), the cumyl spin density is lowest (maximum delocalization), while for the perpendicular conformation ($\theta = 90°$) it is highest (minimum delocalization). Since according to eqn. (1) the *D* value of the triplet diradical **3** is an experimental measure of the spin density for the cumyl radical fragment **2**,[3] the torsional angle θ is readily estimated from Fig. 1 by extrapolation. These values are given as θ_A (method A) in Table 1 for the *ortho*-substituted triplet diradicals **3**. As expected, the torsional angle θ increases with the effective size[9] of the *ortho* groups in the order $H \sim F < Cl < Br \sim CH_3$, except for the *ortho*-fluoro substituent (*cf.* Discussion).

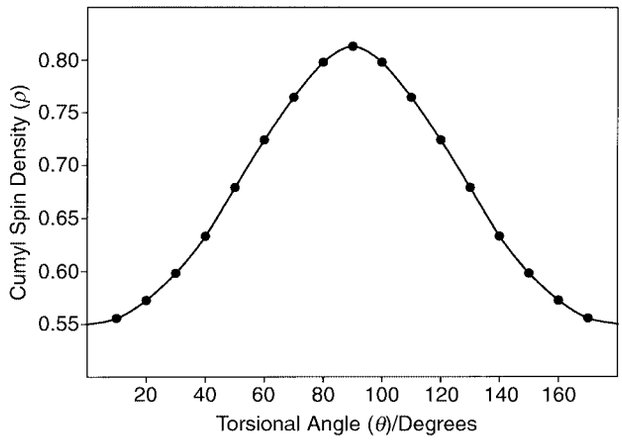


Fig. 1 Calculated (PM3) cumyl spin density (ρ) of the radical **2a** *versus* the torsional angle (θ).

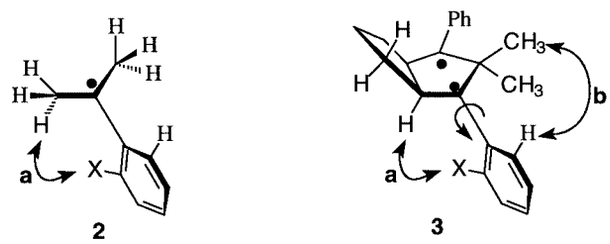


Fig. 2 Possible steric interactions in the cumyl radical **2** and the triplet diradical **3**.

An alternative, but computationally more elaborate task to estimate the torsional angle (θ) is to calculate the minimum-energy conformation of the aryl substituent at the radical center. It will not suffice to consider just the cumyl-radical fragment **2** for this purpose, as becomes apparent when its steric interactions are compared with those in the actual triplet diradicals **3** (Fig. 2). In addition to the steric repulsion between the *ortho* substituent and the cumyl hydrogen atoms (interaction **a** in **2**), there exist effective repulsions **b** in the diradical **3**, whose compromise will result in the final minimum-energy conformation. Hence, the heats of formation for the set of *ortho*-substituted triplet diradicals **3** need to be calculated as a function of the torsional angle to assess the minimum-energy conformation. For this purpose, first the energy change along the reaction coordinate for the rotation of the substituted phenyl ring was calculated by the PM3-AHUF/CI method as described above to acquire the minimum-energy conformer, which was further optimized by an additional UHF/6-31G* calculation.[10] These torsional angles θ_B (method B) of the *ortho*-substituted diradicals are given in Table 1.

Discussion

Already for the parent diradical **3a**, the torsional angle of 50° indicates substantial twisting of the phenyl groups out of the plane of the spin-carrying cyclopentanediyl ring. For the parent cumyl radical **2a** (Fig. 2, X = H), the lowest-energy conform-

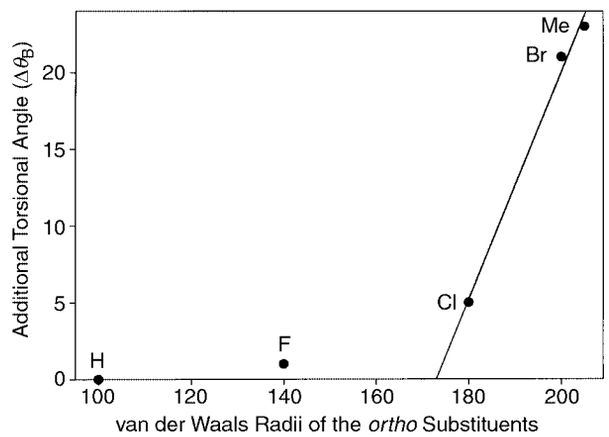


Fig. 3 Calculated torsional angles ($\Delta\theta_B$) in diradicals **3** *versus* the van der Waals radii of the *ortho* substituents.

ation is planar, *i.e.*, the steric repulsion **a** between the methyl and *ortho* hydrogens is insignificant and maximum delocalization of the spin at the cumyl position into the phenyl ring is possible. In contrast, for the rigid cyclopentanediyl triplet diradical **3a** (Fig. 2, X = H), this **a** interaction is significant and the phenyl ring rotates out of planarity to relax this steric repulsion. However, during this rotation, the other *ortho* hydrogen atom of the phenyl group encounters the geminal methyl hydrogen atoms at the 2 position of the cyclopentanediyl ring and this steric interaction **b** prevents further rotation. Thus, the 50° value for the θ_B angle (Table 1) of the parent cyclopentanediyl triplet diradical **3a** (Fig. 2, X = H) is the best compromise between the **a** and **b** repulsions. Relative to the parent diradical **3a**, the $\Delta\theta_B$ values for the other derivatives **3b–e** are also given in Table 1 and allow comparison with the previously acquired θ_A torsional angles for the cumyl radicals **2a**–**e**.

As the data in Table 1 exhibit, the $\Delta\theta_B$ values are slightly higher than θ_A, but the same qualitative trend is obeyed, *i.e.* H ~ F < Cl < Br ~ CH_3, in which the steric effect of the *ortho*-fluoro substituent is again as small as that of a hydrogen atom and that of the *ortho*-bromo one as large as that of the *ortho*-methyl group. A plot of the relative $\Delta\theta$ values *versus* the van der Waals radii[9] of the *ortho* substituents (Fig. 3) reveals that at a threshold value of *ca.* 170 pm, the steric effect of the *ortho* substituent manifests itself by twisting the aryl moiety additionally out of planarity relative to the parent *ortho*-hydrogen-substituted case **3a**. This steric effect diminishes delocalization of the spin at the cumyl position in the triplet diradicals **3**.

The *ortho*-chloro atom is in its effective steric size just slightly above this threshold value and, thus, diradical **3c** ($\Delta\theta$ *ca.* 5°) is essentially as nonplanar as the parent diradical **3a** ($\Delta\theta$ 0°) and the *ortho*-fluoro-substituted derivative **3b** ($\Delta\theta$ *ca.* 1°). In contrast, the bromo- and methyl-substituted cases **3d** and **3e** are by *ca.* 20° more twisted than the parent system **3a** and thereby significantly less delocalized. As a consequence, the more effective the steric effect of the *ortho* substituent, the more twisted is the aryl group from planarity, the more localized the cumyl spin density and, thus, the larger the *D* value, as expected from eqn. (1). This trend may be experimentally assessed by comparison of the *ortho* and *para* substituents. For example, for the fluoro substituent with a negligible steric effect in these cyclopentanediyl triplet diradicals **3**, only the electronic influence should operate. The same *D* values would be expected for the *ortho*- and *para*-fluoro-substituted diradicals, as experimentally confirmed by the identical 0.0514 cm^{-1} value (Table 1). On the contrary, for the sterically demanding bromo and methyl substituents, whose *ortho* regioisomers deviate substantially more from planarity then the parent system (and also the respective *para*-substituted derivatives), the *D* values for the *ortho* isomers **3d** and **3e** are significantly larger than the *para* ones, as experimentally substantiated (Table 1).

It has been demonstrated in this work that the steric demand of an *ortho* substituent has a significant effect on the cumyl spin density in cyclopentanediyl-type triplet diradicals **3** and, consequently, also on the *D* parameter. When the steric size of the substituent is below the threshold value (*ca.* 170 pm), *e.g.*, H and F, no steric effect is observed and the electronic influence of such substituents on the *D* parameter is the same in the *ortho* and *para* positions. For substituents with a steric size above this threshold, *i.e.* Cl, Br and Me, the spin density at the cumyl site is disproportionally increased through twisting out of conjugation and this steric effect surpasses the electronic one. These *ortho*-substituted triplet diradicals show not only *D* values higher than those of the *para*-substituted ones, but also higher than the parent system **3a**. For *meta* and *para* substituents no additional steric effects operate in the triplet diradicals and, thus, the cumyl radical fragment is a good model to account for the observed electronic substituent effects on the cumyl spin density; however, for *ortho* substituents, additional steric effects apply, which makes it necessary to compute the spin densities for the complete triplet diradical species to account for the substituent effects on the experimental *D* parameter.

Experimental

General aspects

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. Infrared spectra were measured on a Perkin-Elmer Infrared Ratio Recording Spectrometer 1420, and UV spectra were run on a Hitachi U 3200 spectrometer. 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 a Polygram Sil G/UV_{254} (40 × 80 mm) instrument 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 **4c**,[11] **4e**,[12] **4f**,[13] **5e**[14] and **5f**[15] are known in the literature and were prepared according to the methods described below.

Preparation of the 1,3-diarylpropane-1,3-diones (4)

Sodium amide (100 mmol) was suspended in 200 ml of dry THF. The corresponding *ortho*-substituted methyl benzoates (50 mmol) and acetophenone (50 mmol) were added under cooling and the resulting mixture was stirred afterwards at *ca.* 20 °C for 16 h. The dark solution was poured on 100 g of crushed ice and acidified with 85% H_3PO_4 (*ca.* 5 ml). The product was extracted with dichloromethane (3 × 100 ml). Drying with $MgSO_4$ and evaporation of the solvent afforded the crude propane-1,3-diones, which were purified by recrystallisation from ethanol or distillation under reduced pressure.

1-(2′-Fluorophenyl)-3-phenylpropane-1,3-dione (4b). 63%, yellow plates, mp 63–64 °C; ν_{max}(KBr)/cm^{-1} 3064, 1595, 1535, 1487, 1286, 1262, 1215; δ_H(250 MHz; $CDCl_3$) 6.99 (s, 1H, enol 2-H), 7.16 (dd, $^3J_{HF}$ = 9.6, ^3J = 8.2, 1H, 3′-H), 7.28 (t, ^3J = 7.3, 1H, 5′-H), 7.45–7.57 (m, 4H, 4′-, 3″-, 4″-, 5″-H), 7.98–8.05 (m, 3H, 6′-, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 97.8 (dd, $^4J_{HF}$ = 11, C-2), 116.5 (dd, $^2J_{HF}$ = 23, C-3′), 123.7 (d, $^2J_{HF}$ = 11, C-1′), 124.5 (dd, $^4J_{HF}$ = 4, C-5′), 127.3 (d, C-2″), 128.6 (d, C-3″), 130.1 (dd, $^3J_{HF}$ = 2, C-6′), 132.6 (d, C-4″), 133.6 (dd, ^3J = 9, C-4′), 135.3 (s, C-1″), 161.1 (d, $^1J_{HF}$ = 255, C-2′), 181.2 (d, $^3J_{HF}$ = 4,

C-1), 186.4 (s, C-3). Anal. Calcd for $C_{15}H_{11}FO_2$ (242.2): C, 74.38; H, 4.58. Found: C, 74.34; H, 4.73%.

1-(2′-Bromophenyl)-3-phenylpropane-1,3-dione (4d). 42%, yellow plates, mp 63–64 °C; ν_{max}(KBr)/cm^{-1} 3010, 2890, 1540, 1450, 1290, 1240, 1170, 1050, 760, 720; δ_H(200 MHz; $CDCl_3$) 6.68 (s, 1H, 2-H), 7.26–7.71 (m, 7H, 3′-, 4′-, 5′-, 6′-, 3″-, 4″-, 5″-H), 7.98 (d, ^3J = 8.3, 2H, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 98.1 (s, C-2), 120.1 (s, C-2′), 127.2 (d, C-2″), 128.5 (d, C-5′), 128.6 (d, C-3″), 129.9 (d, C-6′), 131.6 (d, C-3′), 132.4 (d, C-4″), 133.6 (d, C-4′), 134.6 (s, C-1″), 138.3 (s, C-1′), 183.9 (s, C-1), 188.5 (s, C-3). Anal. Calcd for $C_{15}H_{11}BrO_2$ (303.2): C, 59.42; H, 3.66. Found: C, 59.70; H, 3.69%.

Preparation of the 2,2-dimethyl-1,3-diarylpropane-1,3-diones (5)

Sodium hydride (80 mmol) was suspended in 100 ml of dry toluene. Under cooling, a solution of the corresponding diketone **4** (40 mmol) was added and the solution was stirred for 30 min at *ca*. 20 °C. During a period of 1 h, methyl iodide (120 mmol) was added and afterwards the suspension was heated at about 80 °C for 24 h. After cooling to *ca*. 20 °C, the solution was poured on 200 ml ice and extracted with CH_2Cl_2 (3 × 50 ml). The organic layer was washed with water (100 ml), dried over $MgSO_4$ and the solvent was evaporated (40 °C, 10 Torr). The crude product was purified by recrystallization from cyclohexane or distillation under reduced pressure.

1-(2′-Fluorophenyl)-2,2-dimethyl-3-phenylpropane-1,3-dione (5b). 58%, colorless needles, mp 49–50 °C; ν_{max}(KBr)/cm^{-1} 3080, 2985, 2935, 1651, 1577, 1479, 1448, 1278, 1232, 717; δ_H(200 MHz; $CDCl_3$) 1.63 (s, 6H, 2-CH_3), 6.97 (dd, $^3J_{HF}$ = 9.3, ^3J = 8.2, 1H, 3′-H), 7.10 (t, ^3J = 7.2, 1H, 5′-H), 7.31–7.47 (m, 4H, 4′-, 3″-, 4″-, 5″-H), 7.63 (m, 1H, 6′-H), 7.85 (m, 2H, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 24.3 (q, C-2-CH_3), 61.0 (s, C-2), 116.5 (dd, $^2J_{CF}$ = 23, C-3′), 124.3 (dd, $^4J_{CF}$ = 3, C-5′), 124.9 (d, $^2J_{CF}$ = 13, C-1′), 128.4 (d, C-3″), 129.0 (d, C-2″), 130.4 (dd, $^3J_{CF}$ = 3, C-6′), 132.6 (d, C-4″), 134.0 (dd, $^3J_{CF}$ = 9, C-4′), 136.0 (s, C-1″), 159.8 (d, $^1J_{CF}$ = 255, C-2′), 198.7 (d, $^3J_{CF}$ = 3, C-1), 199.8 (d, $^5J_{CF}$ = 1, C-3). Anal. Calcd for $C_{17}H_{15}FO_2$ (270.3): C, 75.54; H, 5.55. Found: C, 75.95; H, 5.52%.

1-(2′-Chlorophenyl)-2,2-dimethyl-3-phenylpropane-1,3-dione (5c). 43%, colorless needles, mp 55–56 °C; ν_{max}(KBr)/cm^{-1} 3040, 2970, 2910, 1670, 1640, 1550, 1450, 1400, 1240, 1220; δ_H(200 MHz; $CDCl_3$) 1.58 (s, 6H, 2-CH_3), 6.95–7.22 (m, 3H, 3′-, 4′-, 5′-H), 7.28–7.42 (m, 4H, 6′-, 3″-, 4″-, 5″-H), 7.94 (m, 2H, 2″-, 6″-H); δ_C(50 MHz; $CDCl_3$) 23.7 (q, C-2-CH_3), 60.1 (s, C-2), 125.9 (d, C-5′), 128.3 (d, C-3′), 128.7 (d, C-3″), 128.8 (s, C-2′), 129.5 (d, C-2″) ,130.8 (d, C-6′), 131.1 (d, C-4′), 132.6 (d, C-4″), 135.7 (s, C-1″), 137.4 (s, C-1′), 197.8 and 201.5 (2 × s, C-1 and C-3). Anal. Calcd for $C_{17}H_{15}ClO_2$ (286.8): C, 71.21; H, 5.27. Found: C, 71.36; H, 5.13%.

1-(2′-Bromophenyl)-2,2-dimethyl-3-phenylpropane-1,3-dione (5d). 38%, colorless needles, mp 60–61 °C; ν_{max}(KBr)/cm^{-1} 3040, 2980, 2920, 1640, 1570, 1500, 1450, 1400, 1320, 1240; δ_H(200 MHz; $CDCl_3$) 1.58 (s, 6H, 2-CH_3), 7.32–7.41 (m, 2H, 4′-, 5′-H), 7.48–7.54 (m, 3H, 3″-, 4″-, 5″-H), 7.66 (m, 1H, 3′-H), 7.86–7.92 (m, 3H, 6′-, 2″-, 6″-H); δ_C(50 MHz; $CDCl_3$) 24.1 (q, C-2-CH_3), 60.8 (s, C-2), 123.6 (s, C-2′), 127.9 (d, C-5′), 128.5 (d, C-6′), 128.7 (d, C-3″), 129.1 (d, C-2″), 131.3 (d, C-4′), 131.7 (d, C-3′), 133.3 (d, C-4″), 135.4 (d, C-1″), 136.4 (s, C-1′), 197.4 and 202.4 (2 × s, C-1 and C-3). Anal. Calcd for $C_{17}H_{15}BrO_2$ (331.2): C, 61.65; H, 4.56. Found: C, 61.42; H, 4.85%.

Preparation of the 4,4-dimethyl-3,5-diaryl-4*H*-pyrazoles (6)

The corresponding dimethylated diketone **5** (5.00 mmol) was dissolved in 30 ml of $CHCl_3$ and 100% hydrazine hydrate (5.50 mmol) was added. The mixture was refluxed for 24 h. After cooling to *ca*. 20 °C and addition of $MgSO_4$ (2–3 g), the suspension was stirred for 10 min, the solid material removed by filtration and the solvent was evaporated (40 °C, 10 Torr). The crude product was recrystallized from benzene–cyclohexane (1 : 1).

3-(2′-Fluorophenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (6b). 69%, colorless powder, mp 150–151 °C; ν_{max}(KBr)/cm^{-1} 3040, 2980, 2940, 1590, 1520, 1460, 1420, 1310, 1220, 1160; δ_H(200 MHz; $CDCl_3$) 1.55 (s, 6H, 4-CH_3), 7.17–7.29 (m, 2H, 3′-, 5′-H), 7.42–7.52 (m, 4H, 4′-, 3″-, 4″-, 5″-H), 7.69 (m, 1H, 6′-H), 8.05 (m, 2H, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 21.0 (q, C-4-CH_3), 60.6 (s, C-4), 116.4 (dd, $^2J_{CF}$ = 23, C-3′), 118.9 (d, $^2J_{CF}$ = 15, C-1′), 124.3 (dd, $^4J_{CF}$ = 4, C-5′), 127.9 (d, C-2″), 128.7 (d, C-3″), 129.9 (s, C-1″), 130.9 (d, C-4″), 131.0 (dd, $^3J_{CF}$ = 4, C-6′), 131.9 (dd, $^3J_{CF}$ = 9, C-4′), 160.1 (d, $^1J_{CF}$ = 251, C-2′), 178.1 (d, $^3J_{CF}$ = 2, C-3), 178.8 (s, C-5). Anal. Calcd for $C_{17}H_{15}FN_2$ (266.3): C, 76.67; H, 5.68; N, 10.52. Found: C, 76.20; H, 6.07; N, 10.05%.

3-(2′-Chlorophenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (6c). 73%, colorless powder, mp 143–144 °C; ν_{max}(KBr)/cm^{-1} 2981, 1594, 1518, 1491, 1458, 1343, 1070, 1034, 1002, 783; δ_H(200 MHz; $CDCl_3$) 1.53 (s, 6H, 4-CH_3), 7.27 (m, 1H, 5′-H), 7.33–7.43 (m, 2H, 3′-, 4′-H), 7.45–7.56 (m, 4H, 6′-, 3″-, 4″-, 5″-H), 8.06 (m, 2H, 2″-, 6″-H); δ_C(50 MHz; $CDCl_3$) 21.3 (q, C-4-CH_3), 62.1 (s, C-4), 126.4 (d, C-5′), 127.9 (d, C-2″), 128.8 (d, C-3″), 130.0 (d, C-6′), 130.2 (s, C-1″), 130.3 (d, C-3′), 130.5 (s, C-1′), 130.6 (d, C-4″), 131.1 (d, C-4′), 134.8 (s, C-2′), 177.9 and 179.6 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{15}ClN_2$ (282.8): C, 72.21; H, 5.35; N, 9.91. Found: C, 71.85; H, 5.31; N, 9.70%.

3-(2′-Bromophenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (6d). 77%, colorless powder, mp 120–121 °C; ν_{max}(KBr)/cm^{-1} 3040, 2980, 2920, 1570, 1500, 1460, 1430, 1330, 1260, 1210; δ_H(250 MHz; $CDCl_3$) 1.52 (s, 6H, 4-CH_3), 7.24–7.42 (m, 3H, 3′-, 4′-, 5′-H), 7.45–7.53 (m, 3H, 3″-, 4″, 5″-H), 7.72 (m, 1H, 6′-H), 8.08 (m, 2H, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 21.5 (q, C-4-CH_3), 61.8 (s, C-4), 122.9 (s, C-2′), 127.0 (d, C-5′), 127.8 (d, C-2″), 128.9 (d, C-3″), 130.0 (s, C-1″), 130.6 (d, C-4″), 130.8 (d, C-6′), 133.0 (d, C-4′), 133.1 (s, C-3′), 134.1 (d, C-1′), 177.5 and 180.7 (2 × s, C-1 and C-3). Anal. Calcd for $C_{17}H_{15}BrN_2$ (327.2): C, 62.40; H, 4.62; N, 8.56. Found: C, 62.18; H, 4.68; N, 8.85%.

4,4-Dimethyl-3-(2′-methylphenyl)-5-phenyl-4*H*-pyrazole (6e). 81%, colorless powder, mp 110–111 °C; ν_{max}(KBr)/cm^{-1} 2978, 1555, 1519, 1491, 1458, 1342, 1002, 829, 785, 767; δ_H(200 MHz; $CDCl_3$) 1.53 (s, 6H, 4-CH_3), 2.37 (s, 3H, 2′-CH_3), 7.26–7.35 (m, 4H, 3′-, 4′-, 5′-, 6′-H), 7.48–7.53 (m, 3H, 3″-, 4″-, 5″-H), 8.03 (m, 2H, 2″-, 6″-H); δ_C(50 MHz; $CDCl_3$) 20.5 (q, C-4-CH_3), 21.4 (q, C-2′-CH_3), 61.6 (s, C-4), 125.3 (d, C-5′), 127.8 (d, C-2″), 127.9 (d, C-6′), 128.8 (d, C-3″), 129.3 (d, C-3′), 130.2 (d, C-4′), 130.6 (d, C-4″), 130.8 (s, C-1′), 131.0 (s, C-1″), 127.7 (s, C-2′), 177.6 and 181.2 (s, C-3 and C-5). Anal. Calcd for $C_{18}H_{18}N_2$ (262.4): C, 82.41; H, 6.92; N, 10.68. Found: C, 82.04; H, 6.80; N, 10.69%.

3-(2′-Methoxyphenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (6f). 78%, colorless powder, mp 130–131 °C; ν_{max}(KBr)/cm^{-1} 3040, 2960, 2920, 1590, 1510, 1490, 1410, 1250, 1180, 1150; δ_H(200 MHz; $CDCl_3$) 1.39 (s, 6H, 4-CH_3), 3.69 (s, 3H, OCH_3), 6.89–6.99 (m, 2H, 4′-, 5′-H), 7.16–7.53 (m, 4H, 3′-, 3″-, 4″-, 5″-H), 8.04 (m, 3H, 6′-, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 21.3 (q, C-4-CH_3), 55.3 (q, OCH_3), 61.4 (s, C-4), 111.2 (d, C-3′), 111.5 (s, C-1′), 120.3 (d, C-5′), 127.7 (d, C-2″), 128.5 (d, C-6′), 128.6 (d, C-3″), 130.4 (s, C-1″), 130.6 (d, C-4′), 130.9 (d, C-4″), 157.5 (s, C-2′), 178.1 and 180.8 (s, C-3 and C-5). Anal. Calcd for $C_{18}H_{18}N_2O$ (278.4): C, 77.67; H, 6.52; N, 10.06. Found: C, 77.56; H, 6.51; N, 9.77%.

Preparation of the azoalkanes (1)

The corresponding 4*H*-pyrazole **6** (1.00 mmol) and cyclopentene (5.00 mmol) were dissolved in toluene (1 ml). The solution was heated to 110 °C for 2-3 d under high pressure (12.5 kbar). After the solvent was removed (20 °C, 10 Torr), the crude solid product was purified by column chromatography on silica gel.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(2′-fluorophenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1b). 12%, colorless needles, mp 114–115 °C, dec; ν_{max}(KBr)/cm^{-1} 3040, 2940, 2820, 1590, 1570, 1500, 1470, 1420, 1290, 1260; λ_{max} (C_6H_6)/nm 327 (ε/dm^3 mol^{-1} cm^{-1} 27), 349 (95), 362 (167); δ_H(250 MHz; $CDCl_3$) 0.20 (s, 3H, 9-H), 1.03 (s, 3H, 10-H), 1.58–1.62 (m, 6H, 5-, 6-, 7-H), 3.51–3.58 (m, 2H, 4a-, 7a-H), 7.21–7.34 (m, 3H, 3′-, 4′-, 5′-H), 7.48–7.57 (m, 4H, 6′-, 3″-, 4″-, 5″-H), 7.76 (m, 2H, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 17.5 (q, C-9), 18.8 (q, C-10), 25.5 and 25.6 (t, C-5 and C-7), 28.6 (t, C-6), 49.1 (2 × d, C-4a and C-7a), 66.4 (s, C-8), 97.5 (d, $^3J_{CF}$ = 2, C-1), 98.6 (s, C-4), 120.4 (dd, $^2J_{CF}$ = 23, C-3′), 122.8 (dd, $^4J_{CF}$ = 4, C-5′), 123.0 (d, $^2J_{CF}$ = 15, C-1′), 128.3 (d, C-2″), 128.3 (d, C-4″), 129.2 (d, C-3″), 132.9 (dd, $^3J_{CF}$ = 9, C-4′), 135.0 (dd, $^3J_{CF}$ = 4, C-6′), 135.9 (s, C-1″), 164.2 (d, $^1J_{CF}$ = 261, C-2′). Anal. Calcd for $C_{22}H_{23}FN_2$ (334.4): C, 79.02; H, 6.93; N, 8.38. Found: C, 78.96; H, 6.49; N, 8.12%.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(2′-chlorophenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1c). 8%, colorless needles, mp 108–109 °C, dec; ν_{max}(KBr)/cm^{-1} 3030, 2960, 2900, 2820, 1600, 1460, 1430, 1400, 1310, 1240; λ_{max} (C_6H_6)/nm 327 (ε/dm^3 mol^{-1} cm^{-1} 23), 346 (88), 360 (184); δ_H(250 MHz; $CDCl_3$) 0.19 (s, 3H, 9-CH_3), 1.13 (s, 3H, 10-CH_3), 1.46–1.61 (m, 6H, 5-, 6-, 7-H), 3.57 (m, 1H, 4a-H), 4.72 (m, 1H, 7a-H), 7.28–7.33 (m, 3H, 3′-, 4′-, 5′-H), 7.35–7.53 (m, 4H, 6′-, 3″-, 4″-, 5″-H), 7.75 (d, ^3J = 7.3, 2H, 2″-, 6″-H); δ_C(63 MHz; $CDCl_3$) 17.8 (q, C-9), 19.2 (q, C-10), 25.3 and 25.5 (2 × t, C-5 and C-7), 28.7 (t, C-6), 48.8 (d, C-7a), 49.6 (d, C-4a), 67.3 (s, C-8), 98.0 (s, C-4), 99.2 (s, C-1), 126.6 (d, C-5′), 127.5 (d, C-2″), 127.6 (d, C-6′), 127.7 (d, C-4″), 128.3 (d, C-3″), 129.0 (d, C-4′), 130.1 (d, C-3′), 131.8 (s, C-2′), 133.5 (s, C-1′), 135.8 (s, C-1″). Anal. Calcd for $C_{22}H_{23}ClN_2$ (350.9): C, 75.31; H, 6.61; N, 7.98. Found: C, 75.14; H, 6.17; N, 7.62%.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(2′-bromophenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1d). 7%, colorless needles, mp 115–116 °C, dec; ν_{max}(KBr)/cm^{-1} 3020, 2960, 2940, 1890, 1580, 1560, 1460, 1450, 1400, 1280; λ_{max} (C_6H_6)/nm 327 (ε/dm^3 mol^{-1} cm^{-1} 65), 348 (108), 360 (183); δ_H(250 MHz; $CDCl_3$) 0.17 (s, 3H, 9-H), 1.17 (s, 3H, 10-H), 1.60 (m, 6H, 5-, 6-, 7-H), 3.61 (m, 1H, 4a-H), 4.94 (m, 1H, 7a-H), 7.18–7.26 (m, 1H, 4′-H), 7.36–7.54 (m, 4H, 5′-, 3″-, 4″-, 5″-H), 7.68–7.81 (m, 3H, 3′-, 2″-, 6″-H), 8.14–8.18 (m, 1H, 6′-H); δ_C(63 MHz; $CDCl_3$) 17.4 (q, C-9), 19.5 (q, C-10), 25.1 and 25.2 (2 × t, C-5 and C-7), 28.6 (t, C-6), 45.5 (s, C-7a), 49.4 (s, C-4a), 67.5 (s, C-8), 98.0 (s, C-4), 99.7 (s, C-1), 120.8 (s, C-2′), 127.6 (d, C-2″), 128.2 (d, C-4″), 128.8 (d, C-3″), 129.2 (d, C-5′), 129.8 (d, C-4′), 132.6 (d, C-3′), 133.9 (d, C-6′), 135.7 (s, C-1″), 136.1 (s, C-1′). Anal. Calcd for $C_{22}H_{23}BrN_2$ (395.3): C, 66.84; H, 5.86; N, 7.09. Found: C, 67.24; H, 5.44; N, 7.28%.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(2′-methylphenyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1e). 10%, colorless needles, mp 120–121 °C, dec; ν_{max} (KBr)/cm^{-1} 3040, 2980, 2921, 1630, 1555, 1494, 1470, 1446, 1370, 797; λ_{max} (C_6H_6)/nm 327 (ε/dm^3 mol^{-1} cm^{-1} 81), 347 (99), 360 (124); δ_H(200 MHz; $CDCl_3$) 0.20 (s, 3H, 9-CH_3), 1.21 (s, 3H, 10-CH_3), 1.51 (m, 6H, 5-, 6-, 7-H), 2.06 (s, 3H, 2′-CH_3), 3.65 (m, 1H, 4a-H), 4.21 (m, 1H, 7a-H), 7.25 (m, 1H, 5′-H), 7.31–7.46 (m, 5H, 3′-, 4′-, 3″-, 4″-, 5″-H), 7.55 (m, 1H, 6′-H), 7.77 (m, 2H, 2″-, 6″-H); δ_C(50 MHz; $CDCl_3$) 17.1 (q, C-9), 18.7 (q, C-10), 22.7 (q, C-2′-CH_3), 25.7 and 25.8 (t, C-5 and C-7), 28.8 (t, C-6), 47.8 (d, C-7a) 49.0 (d, C-4a), 65.9 (s, C-8) 98.4 (s, C-4), 100.7 (s, C-1), 125.2 (d, C-5′), 125.5 (d, C-6′), 127.6 (d, C-2″), 128.0 (d, C-4″), 128.0 (d, C-4′), 128.4 (d, C-3″), 128.5 (d, C-3′), 136.5 (s, C-2′), 137.2 (s, C-1′), 137.5 (s, C-1″). Anal. Calcd for $C_{23}H_{26}N_2$ (330.5): C, 83.59; H, 7.93; N, 8.48. Found: C, 83.09; H, 7.84; N, 8.22%.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(2′-methoxyphenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (1f). 8%, colorless needles, mp 139–140 °C, dec; ν_{max}(KBr)/cm^{-1} 2958, 2854, 1579, 1490, 1468, 1434, 1371, 1246, 1119, 1022; λ_{max} (C_6H_6)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 121), 363 (152); δ_H(200 MHz; $CDCl_3$) 0.17 (s, 3H, 9-H), 0.99 (s, 3H, 10-H), 1.58 (m, 6H, 5-, 6-, 7-H), 3.51 (m, 1H, 4a-H), 3.84 (s, 3H, OCH_3), 4.22 (m, 1H, 7a-H), 7.01 (dd, ^3J = 8.2, ^4J = 1.2, 1H, 3′-H), 7.10 (dt, ^3J = 7.6, ^4J = 1.2, 1H, 5′-H), 7.34–7.52 (m, 4H, 4′-, 3″-, 4″-, 5″-H), 7.75 (m, 2H, 2″-, 6″-H), 8.14 (dd, ^3J = 7.8, ^4J = 1.7, 1H, 6′-H); δ_C(50 MHz; $CDCl_3$) 17.5 (s, C-9), 18.8 (s, C-10), 25.5 and 25.6 (2 × t, C-5 and C-7), 28.6 (t, C-6), 46.7 (d, C-7a), 49.1 (d, C-4a), 55.0 (q, OCH_3), 66.4 (s, C-8), 97.4 (s, C-1), 98.6 (s, C-4), 111.7 (d, C-3′), 120.6 (d, C-5′), 124.3 (s, C-1′), 127.5 (d, C-2″), 127.6 (d, C-3″), 128.1 (d, C-4″), 128.9 (d, C-6′), 131.4 (d, C-4′), 136.3 (s, C-4″), 158.2 (s, C-2′). Anal. Calcd for $C_{23}H_{26}N_2O$ (346.5): C, 79.73; H, 7.56; N, 8.09. Found: C, 79.37; H, 7.16; N, 7.79%.

EPR Spectroscopy

A solution of the azoalkane **1** (*ca.* 5 μmol) in 2-methyltetrahydrofuran (*ca.* 0.5 mL) was placed into the EPR tube, degassed by purging with argon gas for 15 min, and sealed. The glass matrix was formed by cooling the sample to 77 K with liquid nitrogen. The triplet diradical **2** was generated by irradiation with the 333-, 351- and 364-nm lines of an INNOVA-100 CW argon-ion laser (widened beam, 2.0 W MLUV, 2 min) at 77 K. Its EPR spectrum was recorded on a Bruker ESP-300 spectrometer (9.43 GHz, spectra accumulation with the Bruker 1620 data system, n ⩾ 5). The *D* value was determined by analysis of the Z signals.

Computations

All calculations were run on an IRIS INDIGO Silicon Graphics Workstation. Full geometry optimization of the cumyl radicals **2** was carried out for torsional angles θ of the aryl groups between 0 and 90° by using the PM3[7a] method and AUHF wave functions, which are provided in the VAMP5.0 program.[7b] The cumyl spin densities for different angles θ were then determined with a single-point CI calculation, which results in good spin expectation $\langle S^2 \rangle$ values between 0.75 and 0.78 for these radicals. For geometry optimization of the diradicals **3**, again the minimum-energy conformer was calculated by the PM3-AUHF/CI method as described above. The acquired conformer was then further optimized by the UHF method with the 6-31G* basis set, which is provided by the GAUSSIAN94 program.[10]

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