The *D* parameter (zero-field splitting) as a direct measure of structural and electronic effects in localized triplet 1,3-diradicals

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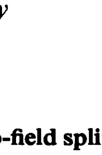
The zero-field splitting parameter *D* of the localized triplet diradicals 3–11, generated in a 2-methyltetrahydrofuran (MTHF) glass matrix at 77 K through photochemical deazetation of the corresponding azoalkanes, have been determined by EPR spectroscopy. It is demonstrated that the *D* parameter depends on structural (changes in the interspin distance *d* between the spin-bearing sites) effects, owing to differing ring size annelation, as well as electronic (changes in the spin density ρ_α at the radical sites) effects, *i.e.* $D = f(d, \rho_\alpha)$. The D_{calcd} values calculated from the theoretical *d* and ρ_α values determined by semiempirical MO calculations (PM3) for the triplet diradicals 1–11, correlate well ($r^2 = 0.961$) with the D_{exp} values determined experimentally. Interestingly, heteroatom substitution at the 4,5-position in the cyclopentane-1,3-diyl moiety causes only a nominal spin delocalization onto the nitrogen atoms for the diradicals 11, which are also classified as localized triplet diradicals.

Introduction

Triplet diradicals are conveniently generated through photochemical deazetation of the corresponding azoalkanes.[1,2] Such intermediates, *e.g.* the prototypes **1** and **2**, are persistent in matrices at temperatures of 4–77 K, detected by EPR spectroscopy[3] and characterized by the zero-field splitting (zfs) parameters *D* and *E*.[2,3] In our recent studies,[4] we have focused attention on the localized triplet diradicals **3** without π conjugation between the radical termini, but substituted at the radical sites with aryl groups capable of spin delocalization. For such triplet 1,3-diradicals we have shown[4b] that the *D* parameter may be described as a simple two-centre interaction between the radical termini, whose magnitude [eqn. (1)]

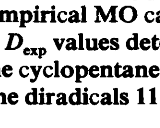
$$D = \frac{3\mu_0 g^2 \mu_B^2}{16\pi}\left(\frac{\rho_A \rho_B}{d_{AB}^3}\right) \qquad (1)$$

depends on the interspin distance d_{AB} and the spin densities ρ_A and ρ_B at the respective radical sites A and B.



1a $R^1 = R^2 = Ph$
1b $R^1 = CH_3$; $R^2 = Ph$

2a $R^1 = R^2 = Ph$; $X^1 = X^2 = H$
2b $R^1 = R^2 = H$; $X^1 = X^2 = H$
2c $R^1 = R^2 = Ph$; $X^1 = X^2 = CH_3$



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The spin density dependence was confirmed experimentally by examining the variations in the *D* parameter for a large set of *meta* and *para* substituents of 1,3-aryl-substituted triplet 1,3-diradicals **3** and **4**.[4b,c] Since spin polarization or captodative stabilization do not play a significant role in localized triplet 1,3-diradicals,[5] the α-spin densities at the radical sites in such triplet diradicals are comparable to those in corresponding monoradicals. Therefore, a good correlation was found between the experimental *D* parameter of the triplet diradicals **3** and the calculated spin densities ρ_α of substituted cumyl radicals, which signifies that 1,3-diaryl-substituted triplet 1,3-diradicals can be depicted as a composite of two geometrically fixed cumyl monoradicals. Hence, the *D* parameter is a sensitive probe for electronic substituent effects through the α spin density dependence at constant d_{AB}.

The aim of the present study was to elucidate geometrical effects on the *D* parameter through variations of the interspin distance d_{AB} at constant spin densities ρ_A and ρ_B. For this purpose, the carbocyclic derivatives **3**–**10** (the structures are given in Table 1) were chosen in which structural variations of the annellating ring at the 4,5-positions of the cyclopentane-1,3-diyl ring were to serve as a vice to change the interspin distance d_{AB}. Furthermore, the effect of heteroatom substitution on the electronic and/or geometric factors was to be probed by determining the *D* values for the urazole-bridged† triplet diradicals **11**. Herein we report the results of our investigation, which demonstrate that the *D* parameter of localized triplet diradicals is dependent on electronic as well as structural effects.

Results

The corresponding azoalkanes were synthesized according to known procedures[6–11] except the azoalkane precursors of the diradicals **1** and **2**, whose *D* parameters were taken from the literature.[5,12,13] The diradicals **3**–**11** were generated in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K by means of irradiation of these azoalkanes with the 364 nm line of an Argon ion laser. All diradicals were persistent at this temperature at least up to 4 h as evidenced by their constant EPR signal. The results of the EPR measurements are summarized in Table 1. The smallest D_{exp} values of the diaryl-substituted, carbocyclic-bridged derivatives were found for the triplet diradicals **5** and **6**, the largest for the heterocyclic-bridged diradicals **9** and **10**. Alkyl substitution directly at the radical site, as in the diradicals **3b** and **3c**, increases substantially the D_{exp} values, while nitrogen

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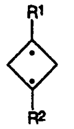
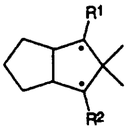
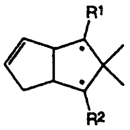
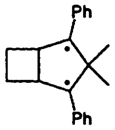
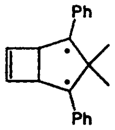
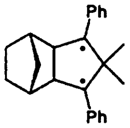
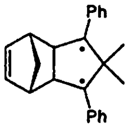
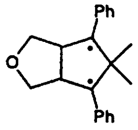
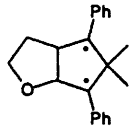
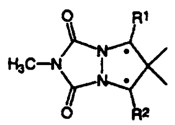
† IUPAC name: urazole = 3,5-dioxo-1,2,4-triazaolidine.

Table 1 Experimental and calculated D values for the triplet 1,3-diradicals **1**–**11**

		R^1	R^2	$\lvert D_{exp}/hc\rvert$[a]/cm^{-1}	$\lvert D_{calc}/hc\rvert$[b]/cm^{-1}	d[c]/pm	ρ_α[c]
	**1a**	Ph	Ph	0.060[d]	0.0585	208.5	0.639
	1b	Ph	CH_3	0.082[d]	0.0776	208.4	0.636/0.850[e]
	**2a**	Ph	Ph	0.047[f]	0.0415	237.1	0.653
	2b	H	H	0.084[f]	0.0781	234.4	0.880
	**2c**			0.049[g]	0.0409	238.6	0.654
	**3a**	Ph	Ph	0.0506	0.0404	239.7	0.654
	3b	Ph	CH_3	0.0671	0.0543	238.1	0.663/0.851[e]
	3c	Ph	$CHCl_2$	0.0630	0.0520	238.0	0.665/0.811[e]
	**4a**	Ph	Ph	0.0504[h]	0.0416	239.8	0.664
	4b	*p*-CN-Ph	*p*-CN-Ph	0.0450[h]	0.0369	240.1	0.627
	4c	*p*-CH_3O-Ph	*p*-CH_3O-Ph	0.0509[h]	0.0420	240.1	0.669
	**5**			0.0479	0.0390	240.8	0.647
	**6**			0.0459	0.0386	241.4	0.646
	**7**			0.0503	0.0399	240.2	0.652
	**8**			0.0491	0.0412	240.3	0.663
	**9**			0.0517	0.0418	239.7	0.665
	**10**			0.0514	0.0417	239.9	0.665
	**11a**	Ph	Ph	0.0452	0.0354	240.9	0.617
	11b	*p*-CN-Ph	*p*-CN-Ph	0.0414	0.0335	240.9	0.600
	11c	*p*-CH_3O-Ph	*p*-CH_3O-Ph	0.0458	0.0365	240.9	0.620
	11d	Ph	CH_3	0.0548	0.0438	238.8	0.614/0.748[e]

[a] Measured in a 2-MeTHF matrix at 77 K, error ± 0.0002 cm^{-1}, $|E/hc| < 0.002$ cm^{-1}. [b] Calculated according to eqn. (1). [c] Values obtained from MO calculations, *cf.* text. [d] Ref. 5. [e] Calculated α spin densities at the methyl-substituted radical centre. [f] Ref. 14. [g] Ref. 13. [h] Ref. 4.

substitution next to the radical centre, as in the urazole-type diradicals **11**, results in a significant decrease (*cf.* Table 1). The previously observed[4] electronic effects of electron-accepting and -donating substituents on the aryl group for carbocyclic derivatives, *e.g.* diradicals **4**, are also reproduced in the corresponding urazole-type diradicals **11**. Thus, a pronounced decrease in the D_{exp} value is manifested for the *p*-CN substituent in **11b** and a significant increase for the *p*-OMe group in **11c** compared with the phenyl derivative **11a** (*cf.* Table 1).

For all triplet diradicals the E parameter was found to be very small ($|E/hc| < 0.002$ cm^{-1}). This is expected for localized triplet diradicals in view of the r^{-5} dependence of the E parameter.[3]

Discussion

The influence of structural features on the D parameter is most prominently displayed by the two diradicals **1a** and **2a**, for which the 1,3-diphenyl substitution provides essentially constant spin densities at the radical sites. Thus, any changes in the D parameter of these triplet diradicals should derive from geometrical effects on the interspin distance d_{AB} [*cf.* eqn. (1)]. *Ab initio* optimized geometries for the parent (H instead of Ph) cyclobutane-1,3-diyldiradical[14] gave an interspin distance of 210 pm and for the parent cyclopentane-1,3-diyldiradical **2b**[15] 237 pm, which accounts nicely for the observed trends in the experimental D values (*cf.* Table 1).

Also all the other carbocyclic bridged derivatives **3–10** (except **3b**, **3c**, **4b** and **4c**) possess 1,3-diphenyl substitution. Hence, for these, constant spin densities at the radical sites may apply as well and changes in the D parameter of these triplet diradicals should derive mainly from effects derived from changes in the interspin distance d_{AB}. As Table 1 reveals, the smallest D_{exp} values are found for the cyclobutene- and cyclobutane-bridged triplet diradicals **6** and **5**. This may be rationalized for the highly strained cyclobutene- and cyclobutane-annellated rings[16] in terms of considerable angle widening in the cyclopentane-1,3-diyl moiety which results in a larger distance d_{AB} and, hence, lower D value. Such a vice effect applies also for the derivatives **7** and **8**, but the influence on the D_{exp} values for the norbornene and norbornane rings are smaller. For the relatively unstrained five-membered ring derivatives **3a**, **4a**, **9** and **10**, the changes in their experimental D values are moderate, which indicates a nominal variation in the interspin distance d_{AB} caused by the cyclopentyl, cyclopentenyl and furanyl annellation.‡

To account for this qualitative trend, we have carried out semiempirical MO calculations (PM3).[17] Indeed, variations in the interspin distance d_{AB} for the aforementioned carbocyclic derivatives are evident (*cf.* Table 1). However, these changes are small, *i.e.* there is only a difference of 2.8 pm between the value (241.4 pm) for the diradical **6** to the smallest value (238.6 pm) for **2c**.

Interestingly, variations in the α spin densities are involved, which indicate that electronic effects are also significant for these bridged carbocyclic derivatives. Thus, angle widening in the cyclopentane-1,3-diyl moiety of these triplet diradicals, which is caused by the angle strain of the annellated rings, will also alter slightly the hybridization at the 4,5-bridgehead carbons. This results in a slight but significant alteration of the hyperconjugation between the radical centre and the β hydrogen, which in turn, results in a change of the α spin densities. However, these are secondary electronic effects, since the differences in the spin densities are not derived from the electronic nature of the substituents at the radical sites, but from the indirect structural modifications.

Besides geometrical effects, primary electronic effects are also expressed in terms of the D parameter. Substitution of a phenyl by a methyl group at the radical site in the triplet diradical **3b** leads to an increase in the D_{exp} value compared with **3a** (0.0671 *versus* 0.0506 cm^{-1}). Owing to the less delocalizing ability of the methyl group, the α spin density is larger at the methyl-substituted radical centre and, hence, a relative increase in the D_{exp} value of 25% is observed. Almost the same relative increase (27%) is found for the D_{exp} values of the cyclobutane-1,3-diyl series[5] **1** (*cf.* Table 1), which accounts nicely for the electronic effects that govern the D parameter. Replacement of the methyl group by the stronger electron-accepting dichloromethyl group, as in the derivative **3c**, decreases again the D_{exp} value (0.0630 cm^{-1}) due to the better spin-accepting property of this group compared with the methyl group.

Significantly, the same trend in the electronic effects is observed experimentally for the urazole-bridged 4,5-diazacyclopentane-1,3-diyl triplet diradicals **11**. Substitution of a phenyl by a methyl group in **11d** results also in an increased D value, but less effectively (18%) compared with the carbocyclic derivatives. These results are in line with the earlier reported[18] D values of *N*-phenylurazole-bridged cyclopentane-1,3-diyl triplet diradicals. Also the known electronic substituent effects for the carbocyclic diradicals **4b** and **4c**[4] are reproduced in the diradicals **11b** and **11c** not only qualitatively but quantitatively (Table 1). For example, the electron-accepting *p*-CN substituent in the triplet diradicals **4b** and **11b** reduces the respective D value by 89 and 91%, while the electron-donating *p*-OMe group increases the D value slightly in the triplet diradicals **4c** and **11c** through spin localization. In this context an interesting case is the diaza derivative **11a** because, although 1,3-diphenyl-substituted, the adjacent nitrogen atoms of the urazole bridge may reduce the spin density at the radical centres. However, the semi-empirical calculations show that for the triplet diradical **11a** compared with the carbocyclic derivative **3a** (cf. Table 1) only 2% of the α spin density is delocalized onto the nitrogen atoms of the urazole moiety. Therefore, the urazole-bridged derivatives **11** are localized triplet diradicals and their lower D value derives from the slightly lower spin densities and the higher interspin distance d_{AB}, the latter a consequence of angle widening due to the shorter N–N *versus* C–C distance (*ca.* 144 *versus* 154 pm[19]).

The semi-empirical calculations, which have been carried out for all triplet diradicals **1–11**, corroborate the general experimental trends of the geometric effects on the interspin distance d_{AB} and electronic substituent effects on the spin density ρ_α (*cf.* Table 1). This is demonstrated by the correlation of the experimental D_{exp} parameters with the computed D_{calcd} values (Fig. 1), obtained according to eqn. (1) from the theoretical d_{AB} and ρ_α values, with the least-squares linear relationship $|D_{exp}/hc| = 0.91 \times |D_{calcd}/hc| + 0.01$ ($r^2 = 0.961$). A similar approach was used for the calculation of zfs parameters for the cyclobutane-1,3-diyl series **1**,[5a] in which Hückel and experimental spin densities (EPR measurements) were employed according to the relationship $D \propto r^{-3}$ (r represents the average distance between the spin density maxima[2]) rather than eqn. (1). The deviation of the slope from unity may derive from the following effects not explicitly considered in our treatment: (*i*) magnetic dipole–dipole interactions between the remaining α spin bearing centres, (*ii*) (α,β) spin–spin interactions due to spin polarization, particularly for the *gem*-dimethyl bridge and (*iii*) the anisotropic term along the *z*-axis. Nevertheless, the present correlation covers such different diradicals as **2**, **3c** or **11** which demonstrates the general applicability of eqn. (1).

In summary, the zfs D parameter of the localized triplet diradicals **3–11** constitutes a valuable spectroscopic tool to assess geometrical (interspin distance d_{AB}) and electronic substituent (spin densities ρ_α) effects in such species. Eqn. (1), which is based on a simple two-centre dipole–dipole interaction,

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‡ The angle strain energies (in kcal mol^{-1}; 1 cal = 4.184 J)[16] are cyclobutene (34.0), cyclobutane (27.4), norbornene (23.6), norbornane (17.0), cyclopentene and cyclopentane (7.0).

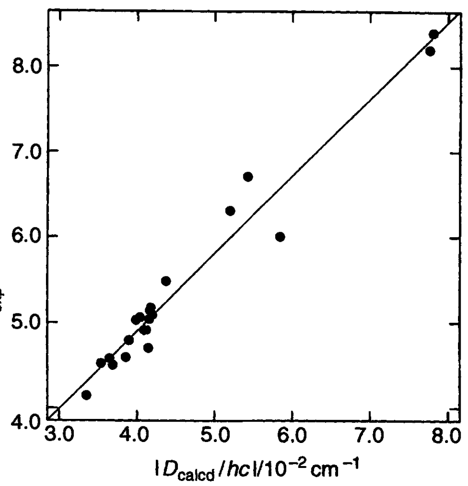

Fig. 1 Correlation of the experimental *D* values against the calculated *D* values of the triplet 1,3-diradicals **1–11**; $r^2 = 0.961$

offers the opportunity to interpret the experimental results through semiempirical MO calculations for a broad variety of structurally different triplet diradicals.

Experimental

Computations

Full geometry optimization of the triplet states of **1–11** were carried out on the highest molecular symmetry§ with planar arrangement of the cyclopentane-1,3-diyl ring and coplanar phenyl groups by using the PM3/OPEN(2,2) method,[17a] which is provided in the VAMP 5.0 program package[20] and run on an IRIS INDIGO Silicon Graphics Workstation. The calculated α spin densities do not consider spin polarization effects, which are known to occur in benzylic systems. Furthermore, the annihilated UHF wave function,[17b] which is also available in the VAMP 5.0 program, seems to overestimate these effects for the α spin densities. The best correspondence with the experimental results was achieved when for the spin densities the mean value of both methods was used.

EPR spectroscopy

A sample (*ca.* 5 × 10^{-4} mmol) of the corresponding azoalkanes was dissolved in 0.3 cm^3 of MTHF, placed into an EPR sample tube (∅ *ca.* 2 mm) and thoroughly degassed by purging with argon gas. The samples were sealed and the 77 K matrix was prepared by freezing the samples in liquid nitrogen. The triplet diradicals **3–11** 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 and 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

^1H and ^{13}C NMR spectra were measured on a Bruker AC 200 (^1H: 200 MHz, ^{13}C: 50 MHz) or on a Bruker 250 spectrometer (^1H: 250 MHz, ^{13}C: 63 MHz) with deuteriochloroform 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 spectrometer. 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 535 and are not corrected. 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 with iodine. Silica gel (63–200 μm; Woelm) was used for column chromatography, the absorbance:substrate ratio was *ca.* 100:1.

1,1-Dichloro-3,3-dimethyl-4-phenylbutane-2,4-dione

In a 100 cm^3, three-necked, round-bottomed flask were placed 2.90 g (15.2 mmol) of 1-phenyl-2,2-dimethylbutane-1,3-dione[8] dissolved in 30 cm^3 of glacial CH_3COOH. The temperature was raised to 70 °C and chlorine gas was passed through the solution for 4 h. The reaction mixture was poured afterwards onto 100 g of cracked ice and stirred for 1 h. After addition of 20 cm^3 of a $Na_2S_2O_3$ solution and 200 cm^3 of CH_2Cl_2, the organic layer was separated and the aqueous layer washed twice with 50 cm^3 CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed at 20 °C and 20 Torr. Recrystallization of the residue from ethanol yielded the diketone as a colourless powder (1.73 g, 44%), mp 47–49 °C (Found: C, 55.43; H, 4.62. $C_{12}H_{12}Cl_2O_2$ requires C, 55.62; H, 4.67%); ν_{max}(KBr)/cm^{-1} 2990, 1720 (CO), 1650 (CO) and 1580; δ_H(200 MHz, $CDCl_3$) 1.62 (6 H, s, CH_3), 6.07 (1 H, s, $CHCl_2$), 7.34–7.58 (3 H, m, arom. H) and 7.74–7.78 (2 H, m, arom. H); δ_C(63 MHz, $CDCl_3$) 23.7 (2 × q), 60.3 (s), 65.6 (d), 128.7 (2 × d), 129.1 (2 × d), 133.4 (d), 135.4 (s) and 197.8 (2 × s).

3-(Dichloromethyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole

The pyrazole was prepared according to literature procedures[8,9] from 130 mg (502 μmol) of 1,1-dichloro-3,3-dimethyl-4-phenylbutane-2,4-dione and 25.1 mg (502 μmol) hydrazine hydrate to afford the 4*H*-pyrazole as a greenish powder (106 mg, 83%), mp 111–112 °C (Found: C, 56.52; H, 4.74; N, 10.84. $C_{12}H_{12}Cl_2N_2$ requires C, 56.49; H, 4.74; N, 10.98%); ν_{max}(KBr)/cm^{-1} 3040, 1655, 1485 and 1455; δ_H(250 MHz, $CDCl_3$) 1.76 (6 H, s, CH_3), 6.83 (1 H, s, $CHCl_2$), 7.48–7.61 (3 H, m, arom. H) and 8.09–8.13 (2 H, m, arom. H); δ_C(63 MHz, $CDCl_3$) 22.9 (2 × q), 61.8 (s), 62.3 (d), 129.1 (2 × d), 129.8 (3 × d), 134.4 (s), 178.2 (s) and 182.4 (s).

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-1-(dichloromethyl)-4-phenyl-8,8-dimethyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine

The unsaturated azoalkane was prepared according to literature procedures[8,9] from 369 mg (1.35 mmol) of 3-(dichloromethyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole, 139 mg (1.22 mmol) CF_3COOH and 7 cm^3 freshly distilled cyclopentadiene to afford a colourless powder (312 mg, 72%), mp 112–114 °C, decomp. (Found: C, 63.39; H, 5.80; N, 8.47. $C_{17}H_{18}Cl_2N_2$ requires C, 63.56; H, 5.65; N, 8.72%); R_f (CH_2Cl_2) 0.45; ν_{max}(KBr)/cm^{-1} 3040, 2960, 2940, 1485 and 1455; δ_H(200 MHz, $CDCl_3$) 0.49 (3 H, s, *endo*-CH_3), 1.07 (3 H, s, *exo*-CH_3), 2.10 (2 H, m, CH_2), 3.61 (1 H, m_c, CH), 4.00 (1 H, m_c, CH), 5.52 (1 H, m_c, olefin H), 5.91 (1 H, m_c, olefin. H), 6.56 (1 H, s, $CHCl_2$), 7.42–7.52 (3 H, m, arom. H) and 7.60–7.67 (2 H, m, arom. H); δ_C(50 MHz, $CDCl_3$) 17.5 (q), 18.9 (q), 31.1 (t), 42.5 (d), 53.1 (d), 63.6 (s), 71.3 (d), 97.5 (s), 96.7 (s), 127.6 (d), 128.1 (2 × d), 128.3 (d), 128.4 (2 × d), 133.8 (s) and 133.9 (d).

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(dichloromethyl)-4-phenyl-8,8-dimethyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine

According to literature procedures,[8,9] 208 mg (647 μmol) of the unsaturated azoalkane gave the saturated derivative as colourless needles (198 mg, 95%), mp 124–126 °C (decomp.) (Found: C, 63.09; H, 6.39; N, 8.46. $C_{17}H_{20}Cl_2N_2$ requires C, 63.16; H, 6.24; N, 8.67%); λ_{max}(C_6H_6)/nm 360 (log ε 2.121); ν_{max}(KBr)/cm^{-1} 2930, 2840, 1480, 1450 and 1010; δ_H(250 MHz, $CDCl_3$) 0.49 (3 H, s, *endo*-CH_3), 1.07 (3 H, s, *exo*-CH_3), 1.20–1.90 (6 H, m, CH_2), 3.42 (2 H, m_c, CH), 6.60 (1 H, s, $CHCl_2$), 7.39–7.49 (3 H, m, arom. H) and 7.57–7.62 (2 H, m, arom. H);

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§ The symmetries are D_{2h} for diradical **1a**, C_{2v} for **2**, C_S for **3a**, **5–8**, **10** and **11a–c** and all others C_1.

δ_C(63 MHz, $CDCl_3$) 15.3 (q), 17.8 (q), 24.7 (t), 26.3 (t), 29.4 (t), 46.2 (d), 48.3 (d), 65.9 (s), 71.7 (d), 96.7 (s), 97.3 (s), 128.0 (2 × d), 128.1 (d), 128.3 (2 × d) and 134.2 (s).

4,10,10-Trimethyl-1,7-(4′-cyanophenyl)-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-en-3,5-dione

According to literature procedures,[11] 390 mg (1.31 mmol) of 3,5-bis(4′-cyanophenyl)-4,4-dimethyl-4*H*-pyrazole[9] and 148 mg (1.31 mmol) 4-methyl-1,2,4-triazolin-3,5-dione gave the azoalkane as a yellow powder (423 mg, 79%), mp >110 °C (decomp.) (Found: C, 63.96; H, 4.18; N, 23.54. $C_{22}H_{17}N_7O_2$ requires C, 64.23; H, 4.17; N, 23.83%); R_f(CH_2Cl_2/$CH_3CO_2CH_3$ 20:1) 0.38; λ_{max}(CH_2Cl_2)/nm 400 and 238 (log ε 2.67 and 4.58); ν_{max}(KBr)/cm^{-1} 3050, 2940, 2220 (CN), 1770, 1705 and 1430; δ_H(200 MHz, $CDCl_3$) 0.34 (3 H, s, *endo*-CH_3), 0.99 (3 H, s, *exo*-CH_3), 2.92 (3 H, s, NCH_3), 7.88 (4 H, dd, J = 8.7, J = 4.7, *ortho*-H) and 8.02 (4 H, dd, J = 8.7, J = 4.7, *meta*-H); δ_C(50 MHz, $CDCl_3$) 14.9 (q), 16.3 (q), 26.1 (q), 60.5 (s), 105.6 (2 × s), 114.6 (2 × s), 118.0 (2 × s), 128.2 (2 × d), 132.5 (2 × d), 132.7 (2 × s) and 156.2 (2 × s).

4,10,10-Trimethyl-1,7-(4′-methoxyphenyl)-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-en-3,5-dione

According to literature procedures,[11] 390 mg (1.26 mmol) of 3,5-bis(4′-methoxyphenyl)-4,4-dimethyl-4*H*-pyrazole[9] and 143 mg (1.26 mmol) of 4-methyl-1,2,4-triazolin-3,5-dione gave the azoalkane as a yellow powder (492 mg, 92%), mp 115–117 °C (decomp.) (Found: C, 63.10; H, 5.46; N, 16.35. $C_{22}H_{23}N_5O_4$ requires C, 62.70; H, 5.50; N, 16.62%); R_f (CH_2Cl_2–$CH_3CO_2CH_3$ 20:1) 0.43; λ_{max}(CH_2Cl_2)/nm 401 and 239 (log ε 2.71 and 4.46); ν_{max}(KBr)/cm^{-1} 2940, 1710, 1705, 1430, 1165 and 1015; δ_H(200 MHz, $CDCl_3$) 0.29 (3 H, s, *endo*-CH_3), 1.10 (3 H, s, *exo*-CH_3), 2.89 (3 H, s, NCH_3), 3.88 (6 H, s, OCH_3), 7.08 (4 H, dd, J = 8.9, J = 4.7, *ortho*-H) and 7.81 (4 H, dd, J = 8.9, J = 4.7, *meta*-H); δ_C(50 MHz, $CDCl_3$) 14.9 (q), 16.4 (q), 25.8 (q), 55.3 (q), 58.7 (s), 106.2 (2 × s), 114.1 (2 × d), 120.1 (2 × s), 128.6 (2 × d), 156.7 (2 × s) and 160.9 (2 × s).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Volkswagen-Stiftung for generous financial support. W. M. N. thanks the Fonds der Chemischen Industrie for a Kékule doctoral fellowship (1992–1994).

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Paper 6/03051C
Received 30th *April* 1996
Accepted 5th *June* 1996