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A Hydrocarbon Hexaradical with Three Localized 1,3-Cyclopentanediyl Triplet Diradicals Linked by 1,3,5-Trimethylenebenzene as Ferromagnetic Coupler: Synthesis of the Azoalkane Precursor, Photochemical Generation of the Polyradical, and EPR Characterization of Its Septet-Spin Ground State

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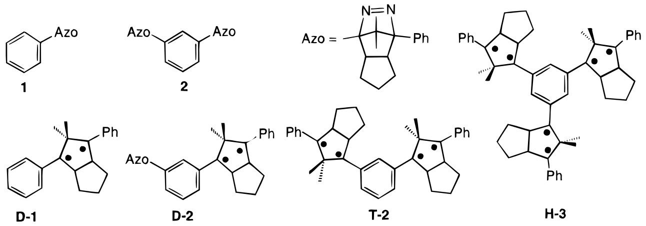
Abstract: The unknown trisazoalkane **3** was prepared and photodenitrogenated into the novel septet hexaradical **H-3**, which is composed of three localized 1,3-cyclopentanediyl triplet diradicals as spin carriers, connected to the cross-conjugated ferromagnetic coupler 1,3,5-trimethylenebenzene. On nitrogen extrusion during the UV photolysis of the trisazoalkane **3** in the toluene matrix at 77 K, the characteristic triplet, quintet, and septet EPR signals for the corresponding diradical **D-3**, tetraradical **T-3**, and hexaradical **H-3** were observed, all persistent for months at 77 K. Computer simulation of the EPR signals for the hexaradical gave the zero-field parameters $D = 0.00907$ cm^{-1} and $E = 0.000187$ cm^{-1}, which is in good agreement with related polyradicals.

Introduction

The study of organic high-spin polyradicals is currently a topical subject, because it paves the way for the design of new magnetic materials.[1] In this context, localized 1,3 diradicals with triplet ground states have received much attention.[2] Particularly cyclopentanediyl diradicals of the type **D-1** have been of interest to us, which may be readily prepared through photodenitrogenation of the corresponding azoalkane **1**.[3] In these open-shell structures, the unpaired spins interact by means of *through-space* and *through-bond* coupling instead of π-type delocalization and, hence, are designated as *localized* diradicals.[3a] Electronic substituent effects on the spin-density distribution, determined experimentally by means of the zero-field D parameter by EPR spectroscopy, and on the spin−orbit coupling, measurable through the triplet lifetimes by time-resolved laser-flash photolysis, have recently provided valuable data on the physical and chemical behavior of these high-spin species.[3b,c]



1 **2** **D-1** **D-2** **T-2** **H-3**

To extend the array of parallel spins, e.g., as in the tetraradical **T-2**,[4] a crucial feature is the ferromagnetic coupler to which the spin-carrying cyclopentadiyl units are attached. An effective choice has been the *m*-phenylene linker, in which cross-conjugation of the two localized triplet-diradical fragments has allowed the quintet-state tetraradical **T-2** to be generated by double photodenitrogenation of the respective bisazoalkane **2**. In principle, the cross-conjugated 1,3,5-trimethylenebenzene ferromagnetic coupler[5] should enable access to the hexaradical **H-3**, in which three localized cyclopentanediyl triplets are attached in the form of the required meta-substitution pattern to ensure the parallel alignment of six electron spins for a septet spin state. For this purpose, the trisazoalkane **3** was prepared and triple photodenitrogenation afforded the hexaradical **H-3**, whose septet spin state was confirmed by EPR spectroscopy.

Results and Discussion

The trisazoalkane **3** was prepared in a seven-step reaction sequence (Scheme 1), in which the key step entailed amine-catalyzed trimerization of the acetylene functionality in dione **6** to generate the central benzene ring in the essential hexaketone **7**.[6] The photolabile azo chromophore was introduced by 3-fold cycloaddition of trisisopyrazole **8** with cyclopentadiene,[7] to

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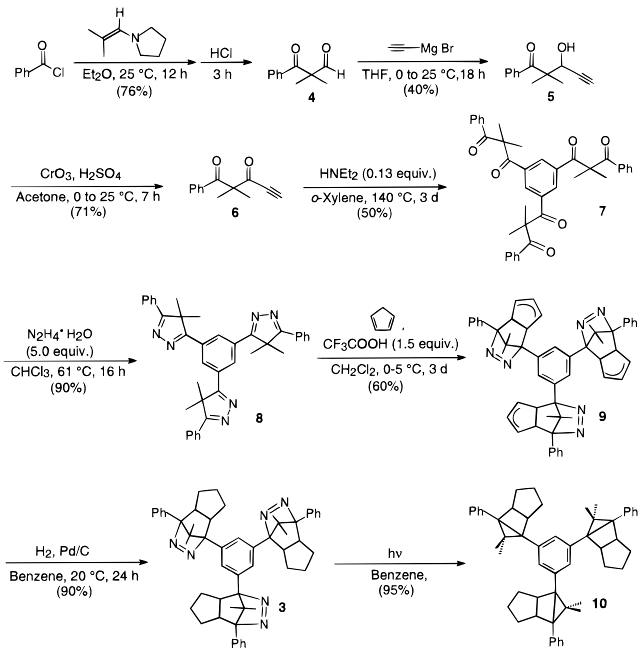
Scheme 1. Synthesis of the Trisazoalkane **3**



afford the unsaturated trisazoalkane **9** followed by catalytic hydrogenation to the required saturated trisazoalkane **3**.

The trisazoalkane **3** possesses essentially the same photochemical properties as the monoazoalkane **1**[8] and the bisazoalkane **2**.[4] Its n,π^*-type azo chromophore absorbs at the same position (363 nm) as the monoazoalkane **1**, except that its intensity is three times larger ($\epsilon = 332\ \mathrm{M^{-1}\ cm^{-1}}$). On photolysis in solution at 364 nm, the trisazoalkane **3** was fully denitrogenated into the trishousane **10**, which consisted of an inseparable mixture of diastereomers. The quantum yield for this nitrogen extrusion ($\phi_{N_2} = 0.35 \pm 0.03$), determined by monitoring spectrophotometrically the conversion of the azoalkane by its absorbance,[8,9] was found to be one-third of that of the monoazoalkane **1** ($\phi_{N_2} = 1.00 \pm 0.10$),[8] employed as actinometer, which signifies that the photodenitrogenation takes place in a stepwise fashion.

The stepwise nitrogen extrusion was also witnessed during the irradiation of the trisazoalkane **3** in a toluene matrix at 77 K at the 333-nm line of the argon-ion laser. The appearance of the stepwise-generated diradical **D-3**, tetraradical **T-3**, and hexaradical **H-3** was monitored by EPR spectroscopy. After an irradiation time of 3 min, the EPR spectrum was virtually superimposable with that of the irradiated bisazoalkane **2** (Figure 1), which gave a mixture of the triplet diradical **D-2** ($D = 0.0507$ cm^{-1}) and quintet tetraradical **T-2** ($D = 0.0116$ cm^{-1}).[4] Consequently, we suggest that after 3 min of irradiation of trisazoalkane **3**, the diradical **D-3** and tetraradical **T-3** were formed. On further irradiation, the signals assigned to the tetraradical **T-3** ($D = 0.0116$ cm^{-1}) grew, but also new signals appeared (Figure 2a). After ca. 10 min of irradiation time, the **T-3** signals stopped growing, while the new signals became more intense.

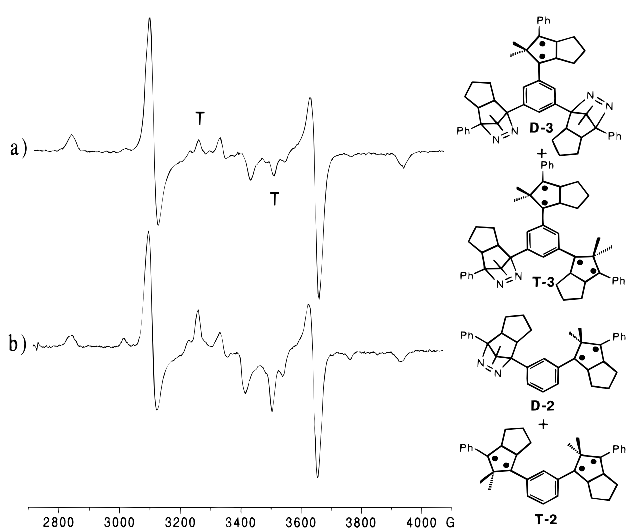


Figure 1. (a) EPR spectrum from the trisazoalkane **3**, assigned to a mixture of the triplet diradical **D-3** and the quintet tetraradical **T-3** (labeled with T); (b) EPR spectrum from the bisazoalkane **2**, assigned to a mixture of the triplet diradical **D-2** and the quintet tetraradical **T-2**.

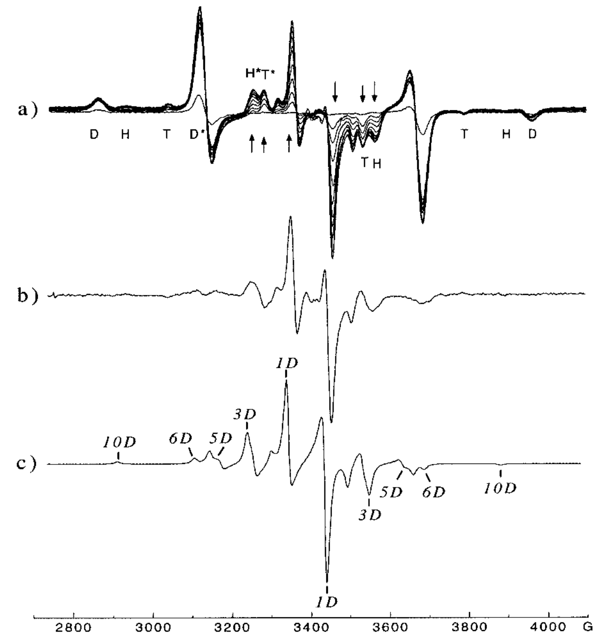


Figure 2. (a) EPR spectra for the irradiation of the trisazoalkane **3** as a function of time; characteristic signals of the diradical **D-3**, the tetraradical **T-3**, and hexaradical **H-3** are labeled with D (D*), T (T*), and H (H*), respectively; the asterisk is used for differentiation of the various signals. (b) Difference spectrum for the subtraction of the diradical and tetraradical contributions from the polyradical spectrum a. (c) Simulation for a septet spin state with $D = 0.00907$ cm^{-1} and $E = 0.000187$ cm^{-1} (ref 10).

The time profile of these characteristic peaks is displayed in Figure 3 and suggests that some of the tetraradical **T-3** is photodenitrogenated to the hexaradical **H-3**. Prolonged irradiation (ca. 60 min total) at 333 nm did not change the ratio of the signal intensities for the diradical, tetraradical, and hexaradical. Irradiation of the trisazoalkane **3** at 351 or 364 nm afforded a polyradical mixture, which contained even less of the hexaradical **H-3**. Therefore, to obtain the clean hexaradical EPR spectrum, spectral subtraction was necessary (Figure 2b). From the doubly integrated *difference* and *total* spectra, the relative amounts of the hexaradical **H-3**, tetraradical **T-3**, and diradical **D-3** were estimated to be about 1:1:2, in a sample of the trisazoalkane **3** that was irradiated at 333 nm for 40 min.

The new signals in Figure 2b were assigned to the hexaradical **H-3** with a septet spin state through simulation of the powder

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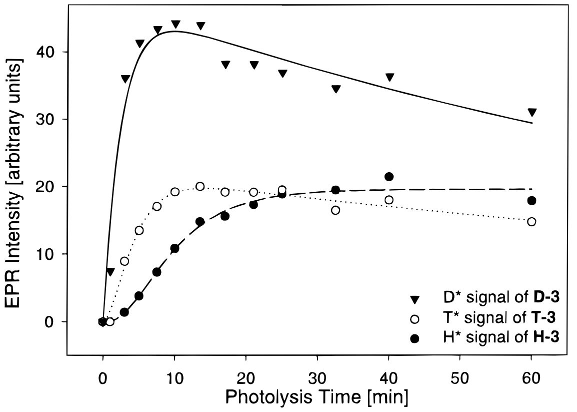

Figure 3. Time profile for the formation of the diradical **D-3**, tetraradical **T-3**, and hexaradical **H-3** during the photolysis of the trisazoalkane **3** at 333 nm; the EPR intensity was determined in terms of the peak height of the corresponding D*, T*, and H* EPR signals (Figure 2a) in the photolysis time of the trisazoalkane **3**.

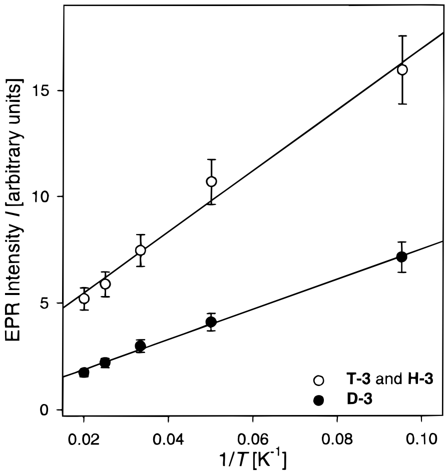

Figure 4. Temperature dependence of the EPR signal intensities (Curie plot) for the diradical **D-3** (3025−3158 G) and the mixture of tetraradical **T-3** and hexaradical **H-3** (3158−3561 G) in toluene in the 10−50 K temperature range.

EPR spectrum by direct diagonalization of the spin Hamiltonian.[10] The best fit between the experimental and simulated spectra (Figure 2) was achieved for the spin Hamiltonian parameters $D = 0.00907$ cm^{-1}, $E = 0.000187$ cm^{-1}, g $\approx$ 2. Unfortunately, in the experimental hexaradical EPR spectrum, the outermost signals, which are definitive to determine the 10D value, are too weak and the D value was estimated from the more intensive and characteristic peaks in the center of the spectrum, which correspond to 3D and 1D. The simulation also disclosed why the characteristic hexaradical signal in the $\Delta m_s = \pm 2$ region was not observed: The difference in the $\Delta m_s = \pm 2$ signals of the tetraradical **T-3** and hexaradical **H-3** is too small and, thus, these half-field signals overlap.

The temperature dependence of the polyradical spectrum was determined by monitoring the EPR intensity of the diradical EPR signals **D-3** and the overlapped tetra- and hexaradical EPR signals **T-3** and **H-3** ($\Delta m_s = \pm 1$ region) in the temperature range 10−50 K (Figure 4). This relatively narrow temperature range is imposed by the fact that microwave saturation of the polyradicals is serious below 10 K, which demanded the use of low microwave power and only weak signals are observed. The resulting plots (Figure 4) of the EPR intensity I versus the inverse temperature $1/T$ are linear for the diradical **D-3**, as well as for the mixture of tetra- and hexaradicals **T-3** and **H-3** and, consequently, the Curie law $I = C/T$ is obeyed. The linearity of the Curie plots (Figure 4), taken together with the fact that at low temperatures (77−10 K) the spectral shape does not change and no new signals appear, signify *high-spin ground states* for the triplet diradical (**D-3)**, quintet tetraradical (**T-3**), and septet hexaradical (**H-3**) species.

Theoretical considerations have suggested that the ratio of the D values for structurally related diradicals (D_{Di}) and triradicals (D_{Tri}) should be constant.[5a,11] This relation was confirmed for a set of *m*-phenylene-coupled diradicals[12] and 1,3,5-trimethylenebenzene-coupled triradicals,[5a] which gave a ratio of $D_{Di}/D_{Tri} = 0.71-0.79$. For the structurally akin tetraradical **T-3** (contains the *m*-phenylene-coupled diradical species) and the hexaradical **H-3** (contains the 1,3,5-trimethylenebenzene-coupled triradical species) their ratio of D values amounts to 0.78, which is in good agreement with the above-mentioned D_{Di}/D_{Tri} ratio. Provided this correspondence is not fortuitous, this fact corroborates our EPR-spectral assignments.

The hexaradical **H-3**, EPR-detected in the polyradical mixture, is as persistent as the diradical **D-1** and tetraradical **T-2**: Even after several months at 77 K, no significant decay of the EPR signal was observed! It persists still at 120 K, but is more reactive than the polybrominated 1,3,5-tris[2-[4-(phenylcarbeno)-phenyl]ethynyl]benzene[5e] (persists even at 140 K) and less reactive than the structurally related 1,3,5-tris(phenylmethylene)-benzene,[5b] a tricarbene, which decomposes already at 97.5 K.

Conclusion

The septet-spin ground state of **H-3** represents the first hexaradical composed of three localized triplet diradicals, namely the spin-carrying 1,3-cyclopentanediyl units, connected to the cross-conjugated ferromagnetic coupler 1,3,5-trimethylenebenzene. Its remarkable persistence (several months at 77 K) encourages the search for other high-spin polyradicals composed of localized spin carriers.

Experimental Section

General Aspects. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AC 200 (^{1}H 200 MHz; ^{13}C 50 MHz) or on a Bruker 250 spectrometer (^{1}H 250 MHz; ^{13}C 63 MHz) with $CDCl_3$ as internal standard; J values are given in Hz. IR spectra of KBr pellets or in CCl_4 were recorded on a Perkin-Elmer 1420 ratio-recording IR spectrophotometer. UV spectra were taken on an Hitachi U 3200 spectrophotometer. Combustion 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 or a Kofler-Mikroheiztisch (C. Reichert AG). TLC spots were identified under a UV lamp. Silica gel (63−200 Fm, Woelm) or basic alumina (activity grade I, Merck) was used for column chromatography; the adsorbant:substrate ratio was ca. 100:1.

2,2-Dimethyl-3-oxo-3-phenylpropionaldehyde (4) was prepared by following the literature procedure.[13]

2,2-Dimethyl-3-hydroxy-1-phenylpent-4-ine-1-one (5). A slow stream of dry acetylene gas was allowed to pass through 100 mL of dry THF with magnetic stirring at 30 °C for 5 min, and a solution of ethylmagnesium bromide [prepared from 2.62 g (108 mmol) of magnesium turnings and 12.9 g (118 mmol) of ethyl bromide in 100 mL of dry THF] was added dropwise under a continuous flow of dry acetylene gas. The resulting solution of ethynylmagnesium bromide

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[10] We are grateful to Dr. Karabunarliev for his computer programm to simulate the EPR spectra of arbitrary spin states ($S = 1-5.5$).

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was cooled to 0 °C and then was added dropwise a solution of 14.1 g (80.0 mmol) of dione **4** in 10 mL of dry THF. After complete addition (ca. 30 min), the reaction mixture was stirred at 20 °C overnight and worked up by adding 350 mL of a cold saturated NH_4Cl solution. The aqueous phase was extracted with ethyl ether (3 × 100 mL) and the combined extracts were dried over anhydrous $MgSO_4$. After evaporation of the solvent (40 °C/760 Torr), the crude product was purified by silica gel chromatography (SiO_2, CH_2Cl_2) to afford 6.77 g (3.35 mmol, 42%) of a colorless oil.

IR (CCl_4): ν = 3280 (C≡C−H), 2950, 1700, 1645, 1530, 1050, 950 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.47 (s, 3H), 1.49 (s, 3H), 2.48 (d, ^4J = 2.2 Hz, 1H), 4.68 (d, ^4J = 1.9 Hz, 1H), 7.48 (m_c, 3H), 7.69 (d, ^3J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.7 (q), 23.2 (q), 51.9 (s), 69.0 (d), 74.3 (d), 82.3 (s), 127.7 (d), 128.2 (d), 131.4 (d), 138,1 (s), 209.1 (s). Anal. Calcd for $C_{13}H_{14}O_2$ (202.3): C, 77.20; H, 6.98. Found: C, 76.85; H, 6.79.

2,2-Dimethyl-1-phenylpent-4-ine-1,3-dione (6). Ten milliliters of Jones reagent,[14] prepared from a 1.6 M solution of CrO_3 in 2.2 M H_2SO_4, was added dropwise to a solution of 2.93 g (14.5 mmol) of **5** in 30 mL of acetone at 0 °C. The reaction mixture was stirred first for 30 min at 0 °C and subsequently for 7.5 h at 20 °C, diluted with 20 mL of distilled water, and extracted with ethyl ether (3 h, 10 mL). The organic phase was washed with saturated $NaHCO_3$ solution (10 mL) and saturated NaCl solution (10 mL) and dried over anhydrous $MgSO_4$. The solvent was removed (40 °C/20 Torr), and silica gel chromatography (SiO_2, CH_2Cl_2) gave 2.19 g (10.9 mmol, 75%) of a colorless oil.

IR (CCl_4): ν 3280 (C≡C−H), 2960, 1670, 1650, 1450, 1060, 960 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.57 (s, 6H), 3.26 (s, 1H), 7.43 (m_c, 3H), 7.77 (d, ^3J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 22.7 (q), 61.4 (s), 79.5 (s), 82.6 (d), 128.6 (d), 129.0 (d), 133.0 (d), 135.2 (s), 188.1 (s), 197.5 (s). Anal. Calcd for $C_{13}H_{12}O_2$ (200.2): C, 77.98; H, 6.04. Found: C, 77.75; H, 6.09.

1,3,5-Tris[2′,2′-dimethyl-1′,3′-dioxo-3′-phenylpropyl]benzene (7). Under an argon-gas atmosphere was added a sample of 88.7 μL (62.1 mg ≡ 0.849 mmol) of freshly distilled diethylamine to a stirred solution of 1.30 g (6.49 mmol) of dione **6** in 10 mL of *o*-xylene and the mixture was heated at reflux for 3 d. The solvent was removed (60 °C/80 Torr), the residual brown oil was purified by silica gel chromatography (SiO_2, CH_2Cl_2), and recrystallization from MeOH gave 641 mg (1.07 mmol, 49%) of colorless needles, mp 108−109 °C.

IR (KBr): ν 2970, 2905, 1670, 1650, 1580, 1430, 1240, 1210, 1150 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.56 (s, 18H), 7.26 (m_c, 9H), 7.65 (d, ^3J = 7.1 Hz, 6H), 8.18 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 24.9 (q), 59.3 (s), 128.6 (d), 129.0 (d), 132.6 (s), 133.0 (d), 135.3 (s), 136.6 (s), 198.7 (s), 198.9 (s). Anal. Calcd for $C_{39}H_{36}O_6$ (600.7): C, 77.98; H, 6.04. Found: C, 78.05; H, 6.13.

1,3,5,-Tris{3′-(4′,4′-dimethyl-5′-phenyl)-[4*H*]-pyrazole}benzene (8). A solution of 501 mg (0.832 mmol) of the hexaketone **7** in 50 mL of $CHCl_3$ was treated with 208 mg (4.16 mmol) of 100% hydrazine hydrate and kept at reflux for 16 h. The reaction mixture was allowed to cool to ca. 20 °C and $MgSO_4$ (ca. 0.5 g) was added. After filtration, the solvent was removed (40 °C/20 Torr), and the crude product was purified by silica gel chromatography (SiO_2, 4:4:1 CH_2Cl_2/ethyl acetate/petroleum ether) to afford 440 mg (0.747 mmol, 90%) of a light yellow powder, mp 235−237 °C.

IR (KBr): ν 2960, 2920, 1510, 1485, 1450, 1430, 1330, 1145 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.85 (s, 18H), 7.55 (m_c, 9H), 8.14 (m_c, 6H), 9.07 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 22.9 (q), 58.9 (s), 128.1 (d), 128.8 (d), 129.0 (d), 129.6 (s), 131.0 (s), 131.2 (d), 177.8 (s), 180.0 (s). Anal. Calcd for $C_{39}H_{36}N_6$ (588.8): C, 79.56; H, 6.16; N, 14.27. Found: C, 79.28; H, 6.25; N, 13.90.

1,3,5-Tris-1′-{(1′α,4′α,4a′α,7a′α)-4′,4a′,7′,7a′-tetrahydro-8′,8′-dimethyl-4′-phenyl-1′,4′-methano-1*H*-cyclopenta[*d*]pyridazine}-benzene (9). A solution of 290 mg (0.493 mmol) of the 4*H*-pyrazole **8** in 30 mL of CH_2Cl_2 was cooled by means of an ice bath and 0.74 mmol of 100% CF_3COOH and 5.0 mL of freshly distilled cyclopentadiene were added. The mixture was stirred for 3 h at ca. 5 °C and kept 3 d at −20 °C. For workup, 0.15 g of potassium carbonate and 0.30 g of silica gel were added, the suspension was stirred for 30 min at ca. 20 °C, the solid was removed by filtration, and the solvent was evaporated (ca. 20 °C/12 Torr). Purification of the crude product by column chromatography (basic Al_2O_3, 5:5:1 CH_2Cl_2/petroleum ether/ethyl acetate) afforded 230 mg (0.293 mmol, 60%) of a colorless powder, mp 166−168 °C dec.

IR (KBr): ν 3050, 2960, 2910, 1595, 1440, 1370, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ =0.21, 0.28 and 0.34 (s, 9H), 1.01, 1.05 and 1.07 (s, 9H), 2.26 (m_c, 6H), 3.69 (m_c, 3H), 4.18 (m_c, 3H), 5.53 (m_c, 6H), 7.49 (m_c, 9H), 7.80 (m_c, 6H), 8.23 (m_c, 3H). ^{13}C NMR ($CDCl_3$): δ 17.2 (q), 17.5 (q), 31.6 (t), 43.2 (d), 58.8 (d), 64.5 (s), 64.6 (s), 97.0 (s), 98.0 (s), 127.2 (d), 127.6 (d), 127.8 (d), 127.9 (d), 128.4 (d), 133.5 (s), 135.7 (2 × s). Anal. Calcd for $C_{54}H_{56}N_6$ (787.1): C, 82.41; H, 6.91; N, 10.68. Found: C, 82.19; H, 7.54; N, 9.71. All attemps to obtain a more satisfactory elemental analysis failed.

1,3,5-Tris-1′-{1′α,4′α,4a′α,7a′α)-4′,4a′,5′,6′,7′,7a′-hexahydro-8′,8′-dimethyl-4′-phenyl-1′,4′-methano-1*H*-cyclopenta[*d*]pyridazine}-benzene (3). A sample of 141 mg (0.180 mmol) of the trisazoalkane **9** was dissolved in 30 mL of benzene and ca. 15 mg of PtO_2 catalyst was added. The reaction mixture was deareated three times by evacuation and flushing with hydrogen gas and saturated with the latter. The hydrogenation was carried out at ca. 20 °C for 24 h under normal pressure. The catalyst was removed by filtration and the solvent evaporated (ca. 20 °C/10 Torr) to afford 136 mg (0.171 mmol, 95%) of a colorless powder, mp 144−145 °C dec.

IR (KBr): 2940, 2850, 1590, 1460, 1440, 1365, 1275, 1015 cm^{-1}. UV (benzene): λ_{max} (ϵ) 329 nm (sh, 160), 351 (sh, 254), 362 (332). ^1H NMR ($CDCl_3$): δ 0.16, 0.23 and 0.29 (s, 9H), 0.97, 1.03 and 1.09 (s, 9H), 1.58 (m_c, 18H), 3.63 (m_c, 6H), 7.46 (m_c, 9H), 7.78 (m_c, 6H), 8.06, 8.16 and 8.21 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 17.3 (q), 18.0 (q), 25.4 (t), 25.5 (t), 28.7 (t), 48.8 (d), 49.0 (d), 66.6 (s), 98.2 (s), 98.5 (s), 98.7 (s), 126.4 (d), 127.5 (d), 127.7 (d), 128.3 (d), 136.2 (2 H, s). Anal. Calcd for $C_{54}H_{60}N_6$ (793.1): C, 81.78; H, 7.62; N, 10.59. Found: C, 81.62; H, 8.06; N, 10.01.

1,3,5-Tris-2′-(3′,3′-dimethyl-4′-phenyltricyclo[3.3.0.0$^{2′,4′}$]octanyl)-benzene (10). A sample of 45.0 mg (0.0570 mmol) of the trisazoalkane **3** was dissolved in 0.6 mL of d^6-benzene, degassed by purging with argon gas, and irradiated (λ = 333−364 nm, 1.3 W, ca. 10 min) until complete consumption, as was confirmed by ^1H NMR analysis. The solvent was removed (40 °C/20 Torr) to yield 38.0 mg (0.0540 mmol, 94%) of colorless solid, mp 145−150 °C (mixture of diastereomers).

IR (KBr): 3055, 2944, 2844, 2857, 1602, 1590, 1496, 1444, 1386, 1024, 697 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.58 and 0.62 (s, 9H), 1.44 and 1.47 (s, 9H), 1.57 (m_c, 12H), 1.99 (m_c, 6H), 2.63 (m_c, 6H), 7.20 (m_c, 18H). ^{13}C NMR ($CDCl_3$): δ 14.7 (q), 22.6 (q), 25.1 (t), 28.4 (t), 29.5 (s), 43.2 (d), 43.6 (d), 44.4 (d), 45.0 (d), 125.4 (d), 127.5 (d), 129.4 (d), 129.8 (d), 138.7 (s). Anal. Calcd for $C_{54}H_{60}$ (709.1): C, 91.47; H, 8.53. Found: C, 91.09; H, 8.57.

EPR Spectroscopy. A sample of ca. 2 mg (2.5 μmol) of the trisazoalkane **3** was dissolved in 0.3 mL of toluene, placed into an EPR sample tube (Ø ca. 2 mm), and thoroughly degassed by purging with a slow stream of dry argon gas. The sample was sealed and the 77 K matrix was prepared by freezing the samples in liquid nitrogen. The polyradical mixture was generated by irradiation with the 333-nm line of an INNOVA-100 CW argon-ion laser (widened beam, 2.4 W, 1−60 min) at 77 K, and the EPR spectra were recorded on a Bruker ESP-300 spectrometer (9.43 GHz), equipped with a variable-temperature accessory and a data-acquisition system. All precautions were taken to avoid undesirable spectral-line broadenings, such as those arising from microwave saturation and magnetic-field overmodulation.

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