The *D* Parameter (EPR Zero-Field Splitting) of Localized 1,3-Cyclopentanediyl Triplet Diradicals as a Measure of Electronic Substituent Effects on the Spin Densities in *Para*-Substituted Benzyl-Type Radicals

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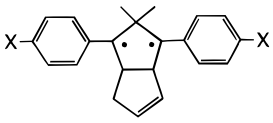
The zero-field splitting parameters *D* of the symmetrically disubstituted and unsymmetrically monosubstituted 1,3-diaryl-1,3-cyclopentanediyl triplet diradicals **1**, **2** (X = *p*-MeO, *p*-Me, *p*-Cl, *p*-NH_2, *p*-CO_2Me, *p*-CN, *p*-NO_2), and **5** were determined in 2-methyltetrahydrofuran glass at 77 K. The linear plot ($m = 0.558$, $r^2 = 0.993$) of the experimental *D* values for the symmetrically disubstituted derivatives *versus* the corresponding monosubstituted ones reveals that the electronic substituent effects are *additive* and implies (except for the magnetic dipolar interaction) that each benzyl-type radical site acts independently in the localized diradicals. This *additivity* permits us to view these triplet diradicals as a composite of the two separate monoradical components and allows us to assess valuable electronic properties of benzyl-type monoradicals from the *D* parameter of the triplet diradical species. A theoretical analysis shows that the *D* parameter is a measure of the spin density ρ at the benzylic positions and the inter-radical distance *d* in localized diradicals. A good correlation exists between the *D* parameter of these triplet diradicals (constant inter-radical distance *d*) and the EPR hyperfine coupling constants of the corresponding benzyl-type monoradicals, which establishes that the observed electronic substituent effects reflect changes in the spin densities at the radical sites. The novel ΔD scale allows us to quantify spectroscopically the *para* substituent effect on the spin delocalization at the benzylic position.

Introduction

The zero-field splitting parameters of triplet states, which are readily determined by EPR spectroscopy under matrix isolation, provide valuable information on the electronic nature of these species through the so-called *D* value and structural data through the symmetry factor *E*.[1] We have recently demonstrated for 1,3-diaryl-1,3-cyclopentanediyl triplet diradicals **1** that the *D* parameter varies with the spin-delocalizing ability of the aryl substituent.[2] It was previously proposed by Dougherty[3]



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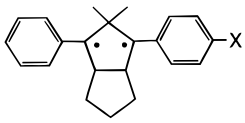
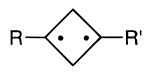


2

1,2	X
a	H
b	F
c	MeO
d	Me
e	Cl
f	NH_2
g	CO_2Me
h	CN
i	NO_2

for the 1,3-cyclobutanediyls **3** that the *D* parameter for *triplet diradicals* reflects the electronic substituent effects in the corresponding *monoradicals*. Consequently, the EPR spectral analysis of tailor-made triplet diradicals may provide valuable information on the electronic properties of monoradicals, *e.g.*, of the aryl-substituted cumyl radicals **4**. In this context, we have defined the



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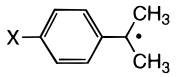

4

R, R' = Me, Et, Ph, Vin

ΔD scale (eq 1),[2] which constitutes a quantitative measure of the spin donor (SD) and spin acceptor (SA)

$$\Delta D = (D_H - D_x)/hc \qquad (1)$$

properties of substituents in localized 1,3-cyclopentanediyl triplet diradicals **1** and provides information on the electronic substituent effects in benzyl-type monoradicals. This novel concept for the evaluation of electronic substituent effects in monoradicals through the *D* parameters of *triplet diradicals* comprises a new spectral method to quantify radical delocalization and hence radical stabilization.[4c] Previously, spectral scrutiny of radical substituent effects could only be assessed through EPR hyperfine coupling constants (a_α or a_β) of *monoradicals*.[4]

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The ΔD scale is based on the assumption that the D parameter describes the magnetic dipole interaction of two electronically *independent* radical centers in a triplet state. A comparison of the ΔD values of the symmetrical diradicals **1** with those of the unsymmetrical derivatives **2** should serve as an appropriate experimental test to assess whether the radical centers in localized triplet diradicals interact sufficiently weakly to be considered as independent monoradicals. At first sight this may seem a paradox, because it is this very interaction that gives rise to the paramagnetic character of triplet states and, thus, provides the opportunity to observe them through EPR spectroscopy. However, it must be recognized that such dipole interaction in triplet diradicals, although spectroscopically significant, is extremely weak (fraction of calories) compared to the energy changes caused by the delocalization power of substituents in monoradicals. The latter happenstance establishes the general validity of the ΔD scale to quantify substituent effects in benzyl-type radicals through the measurement of the D parameter for 1,3-cyclopentanediyl triplet diradicals.

We report herein the EPR results for the symmetrical and unsymmetrical diradicals **1** and **2**, for which, indeed, the anticipated additivity in the ΔD values applies. It is demonstrated in a detailed theoretical analysis that the D parameter serves as a reliable probe of electronic substituent effects through spin density changes. This is confirmed through a correlation between the D parameters with known hyperfine coupling constants.

Results

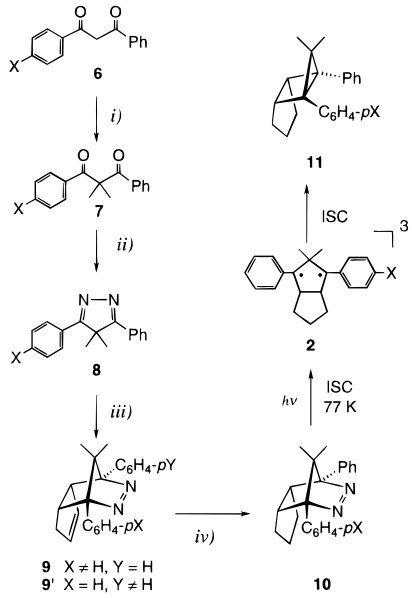
The synthesis of the unsymmetrically substituted azoalkanes (Scheme 1), the precursors of the triplet diradicals **2**, was conducted in analogy to the known synthetic procedure for the symmetrical derivatives.[5] The exclusive products obtained on irradiation of the azoalkanes in $CDCl_3$ solution were the corresponding housane derivatives. For two azoalkanes, the precursors for the diradicals **2f** (*p*-NH_2) and **2i** (*p*-NO_2), some unknown side products (less than 10%) were detected in the NMR spectra, which did not interfere in the analysis of the diradical EPR signals.

The triplet diradicals **1** and **2** were generated by irradiation of the corresponding azoalkanes with the UV lines of an argon ion laser (333, 351, and 363 nm) in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K. The analysis of the Z signals in the EPR spectra afforded the D parameters (Table 1), which are given by one-half of the distance of separation between the low- and high-field turning points; the E parameters were very small (≤ 0.002 cm^{-1}). The data in Table 1 demonstrate that the ΔD parameters of the disubstituted derivatives **1** are about twice as large as those for the monosubstituted diradicals **2**. Although the original set of EPR data referred to the unsaturated derivatives **1**,[2a] the hydrogenation of the C=C double bond in the diradicals **2**, which was performed to eliminate the possibility of regioisomers, has only a slight influence on the D parameter as can be seen from the comparison of the D values for **1a** and **2a**.

In a control experiment to assess matrix effects, the EPR spectra of the triplet diradical **1i** were recorded in MTHF/acetonitrile (2:1) and MTHF/methanol (2:1) glasses. In both matrices the D values (0.0414 cm^{-1}) were the same within experimental errors as for MTHF glass.

The EPR zero-field splitting D parameter of the nitro/methoxy-substituted diradical **5** was determined to assess the possible influence of donor/acceptor substitution. The D parameter of **5** (0.0458 cm^{-1}) falls between those of

Scheme 1. Synthesis of the Azoalkanes 9 and 10 and the Respective Housanes 11



i) MeI, K_2CO_3, *ii)* N_2H_4, *iii)* cyclopentadiene, *iv)* N_2H_2 or H_2 and Pd/C

Table 1. EPR *D* Parameters[a] and ΔD Values of the Triplet Diradicals 1 and 2

		$\lvert D/hc\rvert$ (cm^{-1})		$\Delta D \times 10^{-2}$ (cm^{-1})		$\Delta D \times 10^{-2}$ (cm^{-1})
entry	X	**1**	**2**	**1**	**2**	**2** (calculated)[b]
1b	*p*-F	0.0521[c]		−0.17		−0.08
1c/2c	*p*-MeO	0.0509[e]	0.0509	−0.05	−0.03	−0.02
1a/2a	H	0.0504[c]	0.0506	0.00	0.00	0.00
1d/2d	*p*-Me	0.0502[c]	0.0505	0.02	0.01	0.01
1e/2e	*p*-Cl	0.0495[c]	0.0502	0.09	0.04	0.05
1f/2f	*p*-NH_2	0.0476[c]	0.0493	0.30[d]	0.13	0.14
1g/2g	*p*-CO_2Me	0.0451[c]	0.0479	0.53[e]	0.27	0.27
1h/2h	*p*-CN	0.0450	0.0477	0.54	0.29	0.28
1i/2i	*p*-NO_2	0.0414[c]	0.0454	0.90 (0.91)[d]	0.52	0.47

[a] EPR spectra were recorded at 77 K in a 2-methyltetrahydrofuran matrix; the triplet diradicals **1** and **2** were generated by direct irradiation of the corresponding azoalkanes with the 333-, 351-, and 363-nm lines of a CW argon ion laser. [b] Calculated from the symmetrically substituted triplet diradicals **1** according to eqs 1 and 6. [c] See ref 2a. [d] Measured for the corresponding saturated diradical, see ref 2b. [e] Calculated from the symmetrically substituted triplet diradical **1d** and from the unsymmetrically substituted diradical (*p*-CO_2Me/*p*-Me, $D = 0.0476$ cm^{-1}, ref 2b) according to eq 6.

(4) (a) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2378. (b) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221. (c) Nicholas, A. M. de P.; Arnold, D. E. *Can. J. Chem.* **1986**, *64*, 270. (d) Arnold, D. R.; Nicholas, A. M. de P.; Snow, M. S. *Can. J. Chem.* **1985**, *63*, 1150. (e) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. (f) Korth, H. G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483. (g) Krusic, P. J.; Meakin, P.; Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 6211. (h) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merény, R., Eds.; Reidel: Dordrecht, 1986; p 1.

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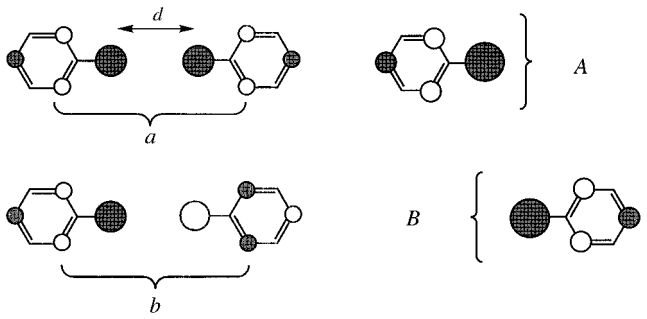
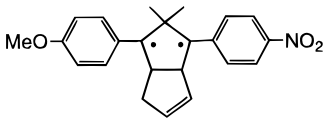


Figure 1. Delocalized π-type NBMOs *a* and *b* and the localized NBMOs *A* and *B* of the benzyl radical fragments as models for the 1,3-cyclopentanediyl diradicals **1**.

the dinitro- and dimethoxy-substituted derivatives **1i** (0.0414 cm^{-1}) and **1c** (0.0509 cm^{-1}).[2]



5
(mixture of regioisomers)

Discussion

Theoretical Considerations. The zero-field splitting parameter *D* of a triplet state originates from the magnetic dipole interaction of the two uncoupled electronic spins (eq 2),[1]

$$D = \left\langle \Phi_k(1,2) \left| \frac{3\mu_0 g^2 \mu_B^2 (r_{1,2}^2 - 3z_{1,2}^2)}{16\pi r_{1,2}^5} \right| \Phi_k(1,2) \right\rangle \quad (2)$$

where

$$\Phi_k(1,2) = \frac{1}{\sqrt{2}}[a(1)b(2) - b(1)a(2)]$$

and

$$a = \frac{1}{\sqrt{2}}(A + B) \quad b = \frac{1}{\sqrt{2}}(A - B)$$

which reside in the two fully delocalized π-type nonbonding molecular orbitals (NBMO) *a* and *b* (Figure 1). Thus, for the symmetrical diradicals **1**, these electron-bearing NBMOs are spread over both benzyl moieties. As to the previously raised question, whether it is legitimate to approximate the dipolar interaction of the two spins in a localized triplet *diradical* by an interaction of two independent benzyl *monoradicals*, these NBMOs are transformed to the two localized benzyl-type MOs *A* and *B*. The overlap integral S_{AB} is nearly zero because of the relative large spatial distance. Substitution of the two delocalized MOs a and b by the two localized MOs *A* and *B* in eq 2 affords eq 3, in which the second term is

$$D = \left\langle A^2(1) \left| \frac{3\mu_0 g^2 \mu_B^2}{16\pi r_{1,2}^3} \right| B^2(2) \right\rangle - \left\langle A(1)B(1) \left| \frac{3\mu_0 g^2 \mu_B^2}{16\pi r_{1,2}^3} \right| A(2)B(2) \right\rangle \quad (3)$$

negligible. The assumption is made that the contribution of anisotropy along the *z* direction is as well depreciable in view of the large spatial separation of the spin centers and the interacting dipoles may be regarded as point charges. Indeed, the first term in eq 3 describes the interaction of electrons which reside in the two given localized MOs *A* and *B* as the origin of the *D* parameter. Magnetic dipole interactions between spin-bearing carbon centers of the particular MO *A* (or MO *B*) are not possible due to the correlation effects of the two α spins. The squares of the atomic orbital coefficients in the normalized MOs *A* and *B* represent spin densities (ρ).[1e] In view of the cubic distance dependence in the perturbation term, the dominant contribution in the dipole interaction derives from the two benzylic positions. Contributions from other carbon atoms, *i.e.*, between the benzylic carbon atom of the MO *A* and the *ortho* carbon atom of the MO *B*, are of minor importance. Thus, with this approximation, eq 3 transforms directly to eq 4, in which *d* is the

$$D = \frac{3\mu_0 g^2 \mu_B^2}{16\pi d^3}\rho^2 \quad (4)$$

spatial distance and ρ is the spin density of the two benzylic carbon atoms. This formula describes the *D* parameter of localized diradicals, in which each radical center bears delocalizing substituents. Equation 4, the extended version of the usually employed eq 5,[6] allows to calculate besides interspin distances the spin densities in localized triplet diradicals.

$$D = \frac{3\mu_0 g^2 \mu_B^2}{8\pi r^3} \quad \text{or} \quad D(\text{cm}^{-1}) = \frac{2.604}{r(\text{Å})^3} \quad (5)$$

Additivity of the Electronic Substituent Effects in Localized 1,3-Diaryl-Substituted 1,3-Cyclopentanediyl Triplet Diradicals. The electronic substituent effects on the *D* parameter in the localized triplet diradicals **1** and **2** (Table 1) are the first of their kind that have been measured.[2] To assess their significance and confirm their validity as a reliable measure of the delocalizing propensity of substituents in such triplet species, it is essential to correlate them with known electronic effects in monoradicals. This condition necessitates one to establish rigorously the initial premise that the triplet diradicals **1** and **2** may be viewed as a composite of two independently active (except for magnetic dipole interaction) benzyl-type (cumyl to be exact) radicals in the rigid, planar 1,3-cyclopentanediyl molecular framework. This premise implies that, for example, in the unsymmetrical triplet diradicals **2** the electronic substituent effect on the *D* parameter is about half that of the symmetrical derivatives **1**. Alternatively, the change in the *D* parameter for the symmetrical triplet diradicals **1** is the sum of the effects measured for the corresponding monosubstituted unsymmetrical cases **2**. This anticipated additivity is, indeed, nicely corroborated when the ΔD values for the symmetrically disubstituted derivatives **1** are compared with the respective ones of the unsymmetrically monosubstituted **2**. A linear plot ($r^2 = 0.993$) is obtained (Figure 2) with a slope $m = 0.558$, *i.e.*, nearly one-half. Thus, the electronic effects on the *D* parameter of localized triplet diradicals are additive and this essential requisite allows us to infer the elec-

(6) Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

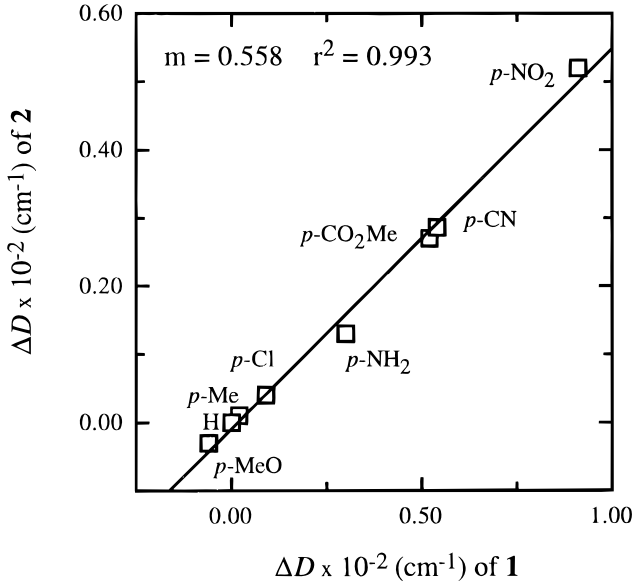


Figure 2. ΔD values of monosubstituted diradicals **2** *versus* those of disubstituted diradicals **1**.

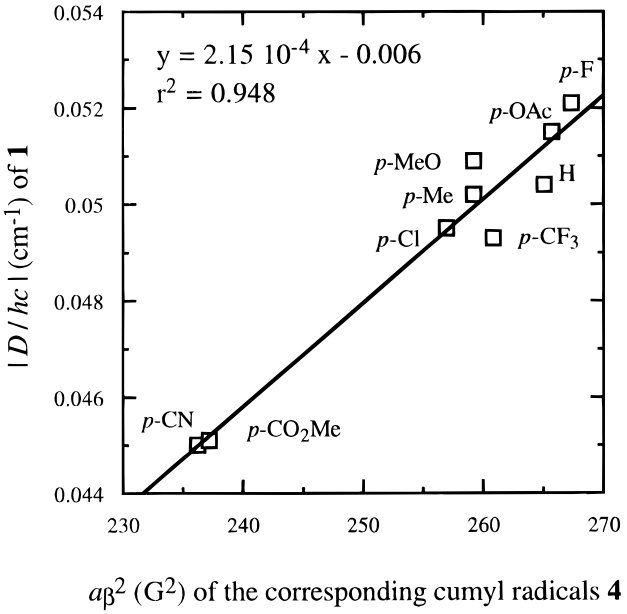


Figure 3. D values of diradicals **1** *versus* hyperfine coupling constants a_β of the corresponding cumyl monoradicals **4**.

tronic properties of monoradicals (cumyl radicals in this case) from the D parameter determined for the 1,3-cyclopentanediyl triplet diradicals.

Spin Densities in Triplet Diradicals as a Measure of Electronic Substituent Effects. The general formula (eq 4) reveals that the magnetic dipolar interaction in triplet states depends on the spin density ρ (electronic effects) and the distance d (geometrical effects) between the radical sites. Since the distance d measures the separation of the two radical carbon atoms, which is expected to be constant in the series of localized diradicals **1** and **2** (*vide infra*), only the ρ factor reflects the electronic substituent effects on the D parameter. In view of the spin-delocalizing properties of the phenyl group, it is expected that the magnetic interaction will be reduced in comparison to radical centers without conjugating groups.[3] For example, the D parameter of the parent 1,3-cyclopentanediyl triplet diradical (no phenyl substituents, $D = 0.084$ cm^{-1})[7a] is much larger than that of its 1,3-diphenyl-disubstituted derivative ($D = 0.045$ cm^{-1}).[7b] Furthermore, *para* substituents in the phenyl groups, which are known[4a–d] to affect the spin density at the benzylic positions through electronic effects, are expected to alter the D parameter. Consequently, for localized triplet diradicals, substituent effects are additive, and with the same separation of the radical sites (constant d in eq 4), the spin density ρ provides a quantitative measure of electron delocalization effects by substituents either directly bound or attached through phenyl-bearing groups at the radical site. Spin-accepting substituents will decrease the spin density, while spin donors increase it. In other words, the ΔD scale (eq 1) derived from the D parameter of 1,3-diaryl-substituted 1,3-cyclopentanediyl triplet diradicals **1** and **2** constitutes a novel spectroscopic probe to assess substituent effects in benzyl-type radicals.

Spin densities (ρ) are theoretical quantities, *i.e.*, they are defined as the sum of the squared coefficients in the NBMO (the molecular orbitals which describe the unpaired electron of the radical site). They are connected to the experimental EPR hyperfine coupling constants (a) through the McConnell equation, namely, $\rho = Qa$,[8] with the proportionality constants $Q_\alpha = 23.04$ G^{-1} and $Q_\beta = 27.74$ G^{-1}.[4h] This relation provides an opportunity to test the spin density dependence of the D parameter (eq 4) of the 1,3-cyclopentanediyl triplet diradicals **1** by comparing them with the known experimental hyperfine coupling constants a_β of the corresponding cumyl radicals.[4d] The semiquadratic correlation ($r^2 = 0.948$) of the experimental D parameter for diradicals **1** with the known hyperfine coupling constants a_β of the corresponding cumyl radicals **4** in Figure 3 is gratifying. An alternative analysis is to employ a double-logarithmic plot in which the slope indicates directly the exponent of a polynomial (x^n) functional dependence. Such a plot affords a slope of 2.2, which is in good agreement with the theoretically expected value of 2.

Although some deviation can be observed for substituents with small delocalizing effects, the strongly delocalizing substituents (*p*-CN and *p*-CO_2Me) correlate well. Unfortunately, no a_β data are available for the *p*-NO_2 and *p*-NH_2 substituents in the cumyl radicals and, consequently, this correlation does not span the full range of possible substituent effects. Inspection of the ΔD values (Table 1) reveals that all *para* substituents, except *p*-MeO and *p*-F, enhance the delocalization of the unpaired electron into the aryl ring. For *p*-MeO and *p*-F, the negative ΔD values signify a higher spin density at the benzyl position than for the unsubstituted case (X = H). These substituents act as spin donors, which is corroborated for the latter by hyperfine coupling EPR data reported for the cumyl monoradical.[4d] Similar spin localization is exercised by the spin donors *p*-OH and *p*-OAc ($\Delta D < 0$).[2c] The spin density is significantly reduced for the strongly conjugating *p*-NO_2, *p*-CN, *p*-CO_2Me, and *p*-NH_2 spin acceptors ($\Delta D > 0$). The

(7) (a) Buchwalter, S. L.; Closs, G. L. *J. Am.Chem. Soc.* **1975**, *97*, 3857. (b) Buchwalter, S. L.; Closs, G. L. *Ibid.* **1975**, *101*, 4688. (c) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753. (d) Adam, W.; Reinhard, G.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1990**, *112*, 4570.

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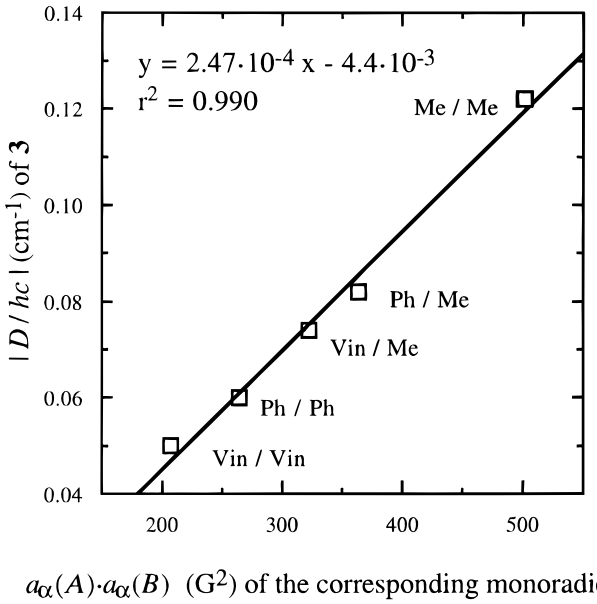

Figure 4. *D* values of diradicals **3** *versus* hyperfine coupling constants a_α of the corresponding monoradicals.

decrease in the ΔD values is expected in view of the delocalizing power of the substituents.[4a−d]

In this context the reported *D* parameters of the 1,3-cyclobutanediyl triplet diradicals **3**[3] are instructive, in which the delocalizing substituents are directly connected to the radical sites. Indeed, the hyperfine coupling constants a_α of the corresponding monoradicals (ethyl,[4e] allyl[4f,g] and phenyl[4b,c]) comprise an excellent ($r^2 = 0.990$) semiquadratic correlation with the *D* parameters of the triplet species **3** (Figure 4).

The above results demonstrate that the *D* values reflect reliably the electronic properties of substituents through the spin density at the radical site in the triplet diradical, a natural consequence of the dipolar interaction between the unpaired electrons. Moreover, besides the EPR hyperfine coupling constants (a_α or a_β) as an experimental measure of spin density in monoradicals, the *D* parameter offers this mechanistically valuable information in triplet diradicals, provided the geometrical factor (*d* dependence in eq 4) is kept constant. We assume that all diradicals **1** and **2** possess the same geometry, which is intuitively expected on the basis of the remote changes in the aryl substituents. Although direct experimental information on this requisite is difficult to acquire, the fact that the same *D* parameter was obtained for the diradical **1i** in three different solvent matrices (MTHF, acetonitrile, methanol) strongly suggests that environmental changes through the matrix material have no measurable influence. In particular, its polar and hydrogen-bonding properties do not play any major role in determining the magnitude of the *D* parameter in such triplet diradicals. Presumably, the similar geometry of the diradicals **1** and **2** is dictated by the inherent conformational preference of the triplet diradical for a planar arrangement of the 1,3-cyclopentanediyl skeleton and compensates the comparably small environmental perturbations by the matrix material. Therefore, the observed substituent effects on the *D* parameter are electronic in origin and the ΔD scale[2] constitutes an experimental *spectroscopic probe* for electron delocalization by substituents in localized triplet diradicals as well as in the corresponding monoradicals.

Let us compare the spin density ρ calculated according to eq 4 for the parent 1,3-diphenyl-1,3-cyclopentanediyl triplet diradical **1a** (X = H) with those for the benzyl or cumyl radical obtained by EPR hyperfine coupling constants. For this comparison, the inter-radical distance *d* is needed, which can be calculated by means of semiempirical methods. We compute[9] with the MNDO/C[10a] (AM1)[10b] method distances of 2.44 (2.41) Å and obtain a ρ value of 0.75 (0.74). From the pertinent experimental data for the benzyl monoradical and from the McConnell equation, the spin density is estimated as $\rho = 0.71$ (a_α = 16.25 G)[4a] and for the cumyl radical as $\rho = 0.59$ (a_β = 16.28 G).[4a] The latter value is smaller than that obtained from the *D* parameter, which can be explained by the fact that the dipolar interaction is not limited to only one two-center interaction, namely, between the two benzylic positions, an approximation that was made to derive eq 4. It is known that spin polarization effects induce α and β spins on atoms adjacent to the radical-bearing centers.[4e,8] An influence on the *D* parameter is only expected if these spins are in the vicinity of both benzylic carbon atoms, which is only the case for the *gem*-dimethyl bridge. The (α/β) spin−spin interaction (with the carbon atom in α position) lowers the *D* value, whereas the (α/α) spin−spin interaction (with carbon atoms in β position) increases the *D* value. Although these secondary effects nearly cancel out, the (α/α) spin−spin may dominate slightly. Nonetheless, the good correlations in Figures 3 and 4 demonstrate that the main two-center interaction dominates and therefore the use of eq 4 to interprete electronic substituent effects in terms of spin density changes is justified.

Due to the additivity of substituent effects (independent radical sites) and the substituent dependence of the spin density ρ, it is now possible to predict the *D* parameter of an unsymmetrically substituted diradical (D_{xy}) if the two *D* parameters for symmetrically substituted diradicals (D_{xx} and D_{yy}) are known. For this purpose eq 6 applies. Since the double bond in diradicals

$$D_{xy} = \frac{3\mu_0 g^2 \mu_B^2}{16\pi d^3}\rho_x\rho_y = \sqrt{D_{xx}D_{yy}} \qquad (6)$$

1 and **2** has only a slight influence on the *D* parameter, the theoretically expected ΔD values of the unsymmetrical diradicals **2** may be calculated from the set of substituent-dependent *D* parameters of the symmetrical diradicals **1** using eqs 1 and 6 (Table 1). A plot of the experimental *versus* the calculated ΔD values for **2** displays an excellent linear correlation ($r^2 = 0.995$).

This analysis was extended to a diradical with a donor/acceptor substitution pattern. The experimental *D* value for the nitro/methoxy-substituted case **5** (0.0458 cm^{-1}) was found to be in excellent agreement with the value calculated from the symmetrical derivatives **1c** and **1i** (0.0459 cm^{-1}). This establishes the absence of any special polar *captodative* effects (push-pull stabilization) in the triplet diradicals of the 1,3-cyclopentanediyl-type. Of course, it must be stressed that these triplet species are localized, a necessary condition that the radical compo-

(9) Calculations were run on a Silicon Graphics Indigo workstation employing the program VAMP 5.0. Rauhut, G.; Alex, A.; Chandrasekhar, J.; Steinke, T.; Clark, T. University of Erlangen−Nürnberg, 1993.

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nents are independent. In contrast, polar effects have a strong influence on the *D* parameters of unsymetrically substituted triplet carbenes.[11]

Conclusion. The theoretical analysis of the magnetic dipole interaction for triplet diradicals shows that the *D* parameter is both a function of the spin densities (ρ) at the radical sites and the inter-radical distance (*d*). Since for the localized 1,3-cyclopentanediyl triplet diradicals the distance factor *d* is constant, the *D* parameter is a sensitive measure of electronic substituent effects through dependence on the spin density factor ρ. The substituent effects are additive, which implies that the electronic effects exerted on each radical site act independent of one another. Thus, valuable information on the delocalizing power of substituents in benzyl-type monoradicals are obtained from the *D* parameters measured for the 1,3-diaryl-substituted 1,3-cyclopentanediyl triplet diradicals **1** and **2**. The fact that the *D* parameter of these localized species correlates well with the known hyperfine coupling constants of the benzyl-type monoradicals establishes that electronic substituent effects are monitored by spin density (ρ) changes. Thus, a new powerful spectroscopic method has become available to assess quantitatively electronic substituent effects in radicals.

Experimental Section

General Aspects. NMR spectra were recorded on a Bruker AC 200 with $CDCl_3$ as solvent and internal standard. Infrared spectra were measured on a Perkin-Elmer 1420 ratio recording infrared (values in cm^{-1}), and UV absorption spectra were aquired on a Hitachi U 3200 spectrophotometer. Melting points were taken on a Reichert Thermovar Kofler apparatus and are not corrected. Combustion analyses were performed by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. Solvents and commercially available chemicals were purified by standard procedures or used as purchased. Column chromatography was carried out on silica gel (0.032−0.063 mm, Woelm). NMR assignments were made on the basis of known spectral data; the specific assignements of the NMR spectra of the regioisomers **9** and **9′** are based on the NMR data for the symmetrically substituted derivatives.[5] ^{1}H NMR coupling constants J_{HH} are given with an accuracy of 0.2 Hz, and ^{13}C NMR multiplicities are derived from DEPT spectra.

EPR Spectroscopy. The particular azoalkanes (ca. 5×10^{-4} mmol) were dissolved in 0.5 mL of 2-methyltetrahydrofuran and placed into an EPR sample tube. After the solution was degassed by purging with argon gas, the sample was sealed and the glass was prepared by freezing the sample with liquid nitrogen. Subsequent irradiation with all UV lines (333, 351, 364 nm) of the CW argon ion laser (INNOVA 100, Coherent Company, widened beam, 1.0 W, 2 min) at 77 K afforded the persistent triplet diradicals **1** and **2**, whose EPR spectra were recorded (spectral accumulation by Bruker DataSystem 1620, $n \geq 5$) on a Bruker ESP-300 spectrometer. The *D* values were determined by analysis of the Z signals.[6]

Preparation of the 1-Aryl-3-phenyl-1,3-propanediones 6. Diones **6c**−**e**,**g** were synthesized in analogy to the literature procedure[5] and purified by recrystallization. To obtain derivatives **6h** and **6i**, 100 mmol of acetophenone and 100 mmol of sodium amide were added to 200 mL of dried diethyl ether, and the formed ammonia was removed by means of a constant nitrogen gas flow for ca. 4 h (monitored by pH indicator). The corresponding *para*-substituted benzoyl chloride (30 mmol) was added slowly, and the mixture was stirred for 30 min at ambient temperature (ca. 25 °C). The reaction mixture was poured onto 200 g of ice, and on addition of 15 mL of acetic acid, dione **6** precipitated.

1-(4′-Methoxyphenyl)-3-phenyl-1,3-propanedione (6c, X = *p*-MeO): 55%, pale yellow needles, mp 127−129 °C (ethanol, lit.[12,13] mp 130 °C).

1-(4′-Methylphenyl)-3-phenyl-1,3-propanedione (6d, X = *p*-Me): 52%, colorless needles, mp 83 °C (ethanol, lit.[12,14] mp 84 °C).

1-(4′-Chlorophenyl)-3-phenyl-1,3-propanedione (6e, X = *p*-Cl): 27%, colorless needles, mp 87−90 °C (ethanol, lit.[12,13a] mp 87 °C).

1-(4′-Carbomethoxyphenyl)-3-phenyl-1,3-propanedione (6g, X = *p*-CO_2Me): 56%, pale yellow needles, mp 123−125 °C (toluene). IR (KBr): $\nu = 3040$ cm^{-1}, 2950, 1720, 1590, 1525, 1430, 1280, 1110, 750, 680. ^{1}H NMR ($CDCl_3$): $\delta = 3.96$ (s, 3H), 6.89 (s, 1H), 7.46−7.63 (m, 3H), 8.01 (dd, $^3J = 7.9$ Hz, $^4J = 1.8$ Hz, 2H), 8.04 (d, $^3J = 8.7$ Hz, 2H), 8.15 (d, $^3J = 8.7$ Hz, 2H), 16.77 (s, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 52.4$ (q), 93.8 (d), 127.0 (d), 127.3 (d), 128.7 (d), 129.8 (d), 132.8 (d), 133.2 (s), 135.4 (s), 139.2 (s), 166.3 (s), 183.4 (s), 187.1 (s). Anal. Calcd for $C_{17}H_{14}O_4$ (282.3): C, 72.33; H, 5.00. Found: C, 72.35; H, 4.93.

1-(4′-Cyanophenyl)-3-phenyl-1,3-propanedione (6h, X = *p*-CN): 40%, yellow needles, mp 152−154 °C (ethanol). IR (KBr): $\nu = 3070$ cm^{-1}, 3040, 2210, 1580, 1535, 1280, 1215, 850, 760, 680. ^{1}H NMR ($CDCl_3$): 6.87 (s, 1H), 7.47−7.64 (m, 3H), 7.79 (d, $^3J = 6.8$ Hz, 2H), 8.00 (dd, $^3J = 6.3$ Hz, $^4J = 1.5$ Hz, 2H), 8.07 (d, $^3J = 6.8$ Hz, 2H), 16.69 (s, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 93.9$ (d), 115.4 (s), 118.1 (s), 127.3 (d), 127.5 (d), 128.8 (d, 132.4 (d), 133.0 (d), 135.1 (s), 139.3 (s), 182.1 (s), 187.5 (s). Anal. Calcd for $C_{16}H_{11}NO_2$ (249.3): C, 77.10; H, 4.45; N, 5.62. Found: C, 77.06; H, 4.68; N, 5.42.

1-(4′-Nitrophenyl)-3-phenyl-1,3-propanedione (6i, X = *p*-NO_2): 38%, yellow needles, mp > 200 °C (lit.[15] mp 160 °C). The product was purified by being washed with chloroform until the wash solution was colorless. Despite the different melting points, NMR spectral data unambiguously established sample identity. ^{1}H NMR (d_6-acetone): $\delta = 6.51$ (s, 1H), 7.34−7.37 (m, 3H), 7.94 (dd, $^3J = 7.3$ Hz, $^4J = 2.4$ Hz, 2H), 8.14 (d, $^3J = 9.2$ Hz, 2H), 8.20 (d, $^3J = 9.2$ Hz, 2H). The enolic hydrogen was not recorded (expected at 16.6 ppm).

General Procedure for the Preparation of the 1-Aryl-2,2-dimethyl-3-phenyl-1,3-propanedione (7). The 2,2-dimethyl-substituted diones **7** were prepared in analogy to the literature procedure.[5] The products were purified by recrystallization.

2,2-Dimethyl-1-(4′-methoxyphenyl)-3-phenyl-1,3-propanedione (7c, X = *p*-MeO): 50%, colorless needles, mp 110−111 °C (methanol). IR (KBr): $\nu = 3040$ cm^{-1}, 2970, 2900, 1660, 1630, 1580, 1250, 1160, 1010, 830. ^{1}H NMR ($CDCl_3$): $\delta = 1.64$ (s, 6H), 3.76 (s, 3H), 6.77 (d, $^3J = 9.0$ Hz, 2H), 7.30 (dd, $^3J = 7.3$ Hz, $^3J = 7.0$ Hz, 2H), 7.41 (dt, $^3J = 7.3$ Hz, $^4J = 1.3$ Hz, 1H), 7.83 (d, $^3J = 9.0$ Hz, 2H), 7.84 (dd, $^3J = 7.0$ Hz, $^4J = 1.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 25.5$ (q), 55.3 (s), 59.2 (q), 113.8 (d), 128.5 (d), 128.5 (s), 129.2 (d), 131.6 (d), 132.9 (d), 135.5 (s), 163.2 (s), 198.6 (s), 200.7 (s). Anal. Calcd for $C_{18}H_{18}O_3$ (282.3): C, 76.57; H, 6.43. Found: C, 76.16; H, 6.61.

2,2-Dimethyl-1-(4′-methylphenyl)-3-phenyl-1,3-propanedione (7d, X = *p*-Me): 44%, colorless needles, mp 124−125 °C (methanol, lit.[16] mp 115 °C). Despite the higher melting points, ^{1}H NMR spectral[15] data established sample identity.

1-(4′-Chlorophenyl)-2,2-dimethyl-3-phenyl-1,3-propanedione (7e, X = *p*-Cl): 31%, colorless needles, mp 105−107 °C (methanol). ^{1}H NMR ($CDCl_3$):[17] $\delta = 1.65$ (s, 6H), 7.28 (d, $^3J = 7.1$ Hz, 2H), 7.32 (dd, $^3J = 6.1$ Hz, $^3J = 5.9$ Hz, 2H), 7.44 (tt, $^3J = 5.9$ Hz, $^4J = 2.2$ Hz, 1H), 7.77 (d, $^3J = 7.1$ Hz, 2H), 7.81 (dd, $^3J = 6.1$ Hz, $^4J = 2.2$ Hz, 2H).

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1-(4′-Carbomethoxyphenyl)-2,2-dimethyl-3-phenyl-1,3-propanedione (7g, X = *p*-CO$_2$Me): 18%, colorless needles, mp 163−164 °C (methanol). IR (KBr): ν = 3060 cm^{-1}, 2980, 2930, 1710, 1640, 1425, 1270, 1100, 940, 700. ^{1}H NMR (CDCl$_3$): δ = 1.67 (s, 6H), 3.88 (s, 3H), 7.31 (dd, ^3J = 7.0 Hz, ^3J = 6.2 Hz, 2H), 7.43 (tt, ^3J = 6.2 Hz, ^4J = 1.4 Hz, 1H), 7.81 (dd, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 2H), 7.86 (d, ^3J = 8.8 Hz, 2H), 7.96 (d, ^3J = 8.8 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 25.2 (q), 52.4 (q), 59.6 (s), 128.7 (d), 129.0 (d), 129.1 (d), 129.7 (d), 133.1 (d), 133.6 (s), 135.4 (s), 138.3 (s), 165.9 (s), 199.8 (s), 199.9 (s). Anal. Calcd for $C_{19}H_{18}O_4$ (310.3): C, 73.53; H, 5.85. Found: C, 73.17; H, 5.67.

1-(4′-Cyanophenyl)-2,2-dimethyl-3-phenyl-1,3-propanedione (7h, X = *p*-CN): 38%, colorless needles, mp 83−85 °C (methanol). IR (KBr): ν = 3050 cm^{-1}, 2970, 2210, 1660, 1645, 1375, 1250, 1230, 940. ^{1}H NMR (CDCl$_3$): δ = 1.67 (s, 6H), 7.33 (dd, ^3J = 7.7 Hz, ^3J = 7.3 Hz, 2H), 7.46 (tt, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H), 7.61 (d, ^3J = 8.4 Hz, 2H), 7.80 (dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz, 2H), 7.90 (d, ^3J = 8.4 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 25.0 (q), 59.6 (s), 116.2 (s), 117.6 (s), 128.7 (d), 129.0 (d), 129.4 (d), 132.4 (d), 133.3 (d), 135.2 (s), 138.4 (s) 199.0 (s), 199.4 (s). Anal. Calcd for $C_{18}H_{15}NO_2$ (277.3): C, 77.96; H, 5.45; N, 5.05. Found: C, 77.79; H, 5.33; N, 4.98.

2,2-Dimethyl-1-(4′-nitrophenyl)-3-phenyl-1,3-propanedione (7i, X = *p*-NO$_2$): 27%, pale yellow needles, mp 140−141 °C (methanol). IR (KBr): ν = 3060 cm^{-1}, 2980, 2920, 1650, 1520, 1340, 1250, 1220, 940, 700. ^{1}H NMR (CDCl$_3$): δ = 1.69 (s, 6H), 7.33 (dd, ^3J = 7.3 Hz, ^3J = 7.0 Hz, 2H), 7.46 (tt, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H), 7.81 (dd, ^3J = 7.0 Hz, ^4J = 1.4 Hz, 2H), 7.97 (d, ^3J = 8.1 Hz, 2H), 8.15 (d, ^3J = 8.1 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 25.1 (q), 59.8 (s), 123.8 (d), 128.9 (d), 129.1 (d), 130.1 (d), 133.5 (d), 135.3 (s), 140.0 (s), 149.9 (s), 198.9 (s), 199.4 (s). Anal. Calcd for $C_{17}H_{15}NO_4$ (297.3): C, 68.68; H, 5.09; N, 4.71. Found: C, 68.64; H, 4.86; N, 4.53.

General Procedure for the Preparation of the 3-Aryl-4,4-dimethyl-5-phenylisopyrazole (8). The pyrazoles **8** were prepared in analogy to the literature procedure.[5] The products were purified by recrystallization. The derivatives **8h** and **8i** required heating at 130 °C and 0.5 Torr for 3 h to quantitatively remove water.

4,4-Dimethyl-3-(4′-methoxyphenyl)-5-phenyl-4*H*-pyrazole (8c, X = *p*-MeO): 55%, colorless needles, mp 154−155 °C (cyclohexane). IR (KBr): ν = 3045 cm^{-1}, 2960, 1590, 1505, 1495, 1405, 1245, 1175, 1025, 825. ^{1}H NMR (CDCl$_3$): δ = 1.69 (s, 6H), 3.87 (s, 3H), 7.01 (d, ^3J = 9.1 Hz, 2H), 7.45−7.52 (m, 3H), 8.04−8.10 (m, 4H). ^{13}C NMR (CDCl$_3$): δ = 23.0 (q), 55.4 (q), 58.2 (s), 114.2 (d), 122.4 (s), 127.7 (d), 128.7 (d), 129.5 (d), 130.1 (s), 130.5 (d), 161.6 (s), 178.3 (s), 178.4 (s). Anal. Calcd for $C_{18}H_{18}N_2O$ (278.4): C, 77.67; H, 6.52; N, 10.06. Found: C, 77.37; H, 6.43; N, 9.86.

4,4-Dimethyl-3-(4′-methylphenyl)-5-phenyl-4*H*-pyrazole (8d, X = *p*-Me): 75%, colorless needles, mp 135−136 °C (cyclohexane). IR (KBr): ν = 3045 cm^{-1}, 2950, 1595, 1510, 1490, 1440, 1340, 1150, 1000, 820, 770, 690. ^{1}H NMR (CDCl$_3$): δ = 1.70 (s, 6H), 2.43 (s, 3H), 7.30 (d, ^3J = 8.5 Hz, 2H), 7.46−7.52 (m, 3H), 7.98 (d, ^3J = 8.5 Hz, 2H), 8.06 (dd, ^3J = 5.6 Hz, ^4J = 3.0 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 21.4 (q), 22.9 (q), 58.5 (s), 127.1 (s), 127.8 (s), 127.8 (s), 128.7 (d), 129.5 (d), 130.1 (s), 130.6 (d), 141.2 (s), 178.7 (s), 178.9 (s). Anal. Calcd for $C_{18}H_{18}N_2$ (262.4): C, 82.41; H, 6.92; N, 10.68. Found: C, 82.32; H, 6.61; N, 10.53.

3-(4′-Chlorophenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (8e, X = *p*-Cl): 51%, colorless needles, mp 155−156 °C (cyclohexane). IR (KBr): ν = 2950 cm^{-1}, 2910, 1575, 1510, 1475, 1450, 1380, 1330, 1080, 995, 815, 770, 695. ^{1}H NMR (CDCl$_3$): δ = 1.69 (s, 6H), 7.47 (d, ^3J = 8.9 Hz, 2H), 7.47−7.53 (m, 3H), 8.02 (d, ^3J = 8.9 Hz, 2H), 8.07 (dd, ^3J = 5.5 Hz, ^4J = 3.0 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 22.7 (q), 58.6 (s), 127.7 (d), 128.4 (s), 128.8 (d), 129.1 (d), 129.1 (d), 129.6 (s), 130.9 (d), 137.0 (s), 178.0 (s), 179.1 (s). Anal. Calcd for $C_{17}H_{15}N_2Cl$ (282.8): C, 72.21; H, 5.35; N, 9.91. Found: C, 71.97; H, 5.42; N, 9.91.

3-(4′-Carbomethoxyphenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (8g, X = *p*-CO$_2$Me): 61%, colorless needles, mp 181−182 °C (cyclohexane). IR (KBr): ν = 3040 cm^{-1}, 2980, 2930, 1710, 1595, 1510, 1430, 1270, 1100, 770, 755. ^{1}H NMR (CDCl$_3$): δ = 1.71 (s, 6H), 3.95 (s, 3H,), 7.47−7.54 (m, 3H), 8.08 (dd, ^3J = 5.4 Hz, ^4J = 3.0 Hz, 2H), 8.14 (s, 2H), 8.14 (s, 2H). ^{13}C NMR (CDCl$_3$): δ = 22.6 (q), 52.4 (q), 58.8 (s), 127.8 (d), 128.0 (d), 128.9 (d), 129.7 (s), 129.9 (d), 131.1 (d), 131.8 (s), 134.0 (s), 166.4 (s), 178.2 (s), 179.5 (s). Anal. Calcd for $C_{19}H_{18}N_2O_2$ (306.4): C, 74.49; H, 5.92; N, 9.14. Found: C, 74.27; H, 5.87; N, 9.13.

3-(4′-Cyanophenyl)-4,4-dimethyl-5-phenyl-4*H*-pyrazole (8h, X = *p*-CN): 85%, yellow needles, mp 184−185 °C (cyclohexane). IR (KBr): ν = 2960 cm^{-1}, 2920, 2210, 1590, 1510, 1485, 1450, 1340, 1000, 835, 780, 700. ^{1}H NMR (CDCl$_3$): δ = 1.71 (s, 6H), 7.48−7.55 (m, 3H), 7.79 (d, ^3J = 8.6 Hz, 2H), 8.08 (dd, ^3J = 5.5 Hz, ^4J = 2.2 Hz, 2H), 8.19 (d, ^3J = 8.6 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 22.5 (q), 58.6 (s), 114.0 (s), 118.2 (s), 128.0 (d), 128.2 (d), 128.9 (d), 129.3 (s), 131.2 (d), 132.5 (d), 133.9 (s), 177.3 (s), 179.9 (s). Anal. Calcd for $C_{18}H_{15}N_3$ (273.3): C, 79.10; H, 5.53; N, 15.37. Found: C, 78.84; H, 5.84; N, 15.23.

4,4-Dimethyl-3-(4′-nitrophenyl)-5-phenyl-4*H*-pyrazole (8i, X = *p*-NO$_2$): 51%, yellow needles, mp 237−238 °C. IR (KBr): ν = 3100 cm^{-1}, 2970, 1585, 1520, 1505, 1330, 1100, 995, 850, 775, 700. ^{1}H NMR (CDCl$_3$): δ = 1.72 (s, 6H), 7.49−7.53 (m, 3H), 8.08 (dd, ^3J = 5.5 Hz, ^4J = 3.1 Hz, 2H), 8.25 (d, ^3J = 9.1 Hz, 2H), 8.34 (d, ^3J = 9.1 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 22.5 (q), 58.8 (s), 123.9 (d), 128.1 (d), 128.6 (d), 128.9 (d), 129.4 (s), 131.4 (d), 135.8 (s), 148.8 (s), 177.1 (s), 180.0 (s). Anal. Calcd for $C_{17}H_{15}N_3O_2$ (293.3): C, 69.61; H, 5.15; N, 14.33. Found: C, 69.82; H, 5.11; N, 14.34.

General Procedure for the Preparation of the Azoalkanes 9. The azoalkanes were prepared in analogy to the literature procedure[5] and were purified by column chromatography. The eluated azoalkane solution had to be filtered through solid potassium carbonate to remove traces of acids, since the latter catalyzes retro-Diels−Alder reactions. In all cases a mixture of two regioisomeres (ca. 1:1) were obtained.

(1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-methoxyphenyl)-4-phenyl- [9c, X = *p*-MeO, Y = H] and (1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-4-(4′-methoxyphenyl)-1-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine [9c′, X = H, Y = *p*-MeO]: 40%, colorless needles, mp 156−157 °C dec, R_f = 0.10 (silica gel, methylene chloride). IR (KBr): ν = 3020 cm^{-1}, 2900, 1595, 1560, 1500, 1440, 1420, 1290, 1240, 1170, 1025, 1010, 810, 790. UV (benzene): λ_{max} (ϵ) 329 nm (sh, 26), 352 (sh, 97), 361 (170). Anal. Calcd for $C_{23}H_{24}N_2O$ (344.5): C, 80.20; H, 7.02; N, 8.13. Found: C, 79.78; H, 6.80; N, 8.00.

Isomer 9c. ^{1}H NMR (CDCl$_3$): δ = 0.20 (s, 3H), 0.99 (s, 3H), 2.21 (d, ^3J = 7.3 Hz, 2H), 3.64 (ddd, ^3J = ^3J = 7.3 Hz, ^3J = 4.7 Hz, 1H), 3.87 (s, 3H), 4.06 (d, ^3J = 4.7 Hz, 1H), 5.50 (s, 2H,), 7.04 (d, ^3J = 8.8 Hz, 2H), 7.40−7.54 (m, 3H), 7.71 (d, ^3J = 8.8 Hz, 2H), 7.77 (dd, ^3J = 8.2 Hz, ^3J = 1.5 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 17.0 (q), 17.3 (q), 31.6 (t), 43.1 (d), 55.2 (s), 56.6 (d), 64.0 (s), 96.6 (s), 97.7 (s), 113.7 (d), 127.1 (d), 127.2 (d), 127.8 (d), 127.8 (s), 128.3 (d), 128.7 (d), 133.4 (d), 135.9 (s), 159.1 (s).

Isomer 9c′. ^{1}H NMR (CDCl$_3$): δ = 0.20 (s, 3H), 0.99 (s, 3H), 2.22 (d, ^3J = 7.0 Hz, 2H), 3.60 (ddd, ^3J = ^3J = 7.0 Hz, ^3J = 4.7 Hz, 1H), 3.87 (s, 3H), 4.10 (d, ^3J = 4.7 Hz, 1H), 5.50 (s, 2H), 7.03 (d, ^3J = 8.8 Hz, 2H), 7.40−7.54 (m, 3H), 7.69 (d, ^3J = 8.8 Hz, 2H), 7.79 (dd, ^3J = 8.2 Hz, ^3J = 1.5 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ = 17.0 (q), 17.3 (q), 31.6 (t), 43.0 (d), 55.2 (s), 56.6 (d), 64.0 (s), 96.6 (s), 97.7 (s), 113.7 (d), 127.2 (d), 127.5 (d), 127.7 (d), 127.9 (s), 128.3 (d), 128.3 (d), 133.5 (d), 135.9 (s), 159.2 (s).

(1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-methylphenyl)-4-phenyl- [9d, X = *p*-Me, Y = H] and (1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-phenyl-4-(4′-methylphenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [9d′, X = H, Y = *p*-Me]: 61%, colorless needles, mp 145−147 °C dec, R_f = 0.23 (silica gel, methylene chloride). IR (KBr): ν = 3010 cm^{-1}, 2930, 2900, 1575, 1500, 1495, 1450, 1430, 1360, 1290, 1010, 805, 750, 730, 715, 695. UV (benzene): λ_{max} (ϵ) 329 nm (sh, 45), 350 (sh, 107), 361 (179). Anal. Calcd for $C_{23}H_{24}N_2$ (328.5): C, 84.11; H, 7.36; N, 8.53. Found: C, 83.70; H, 7.78; N, 8.21.

Isomer 9d. ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3H), 1.01 (s, 3H), 2.22 (d, ^3J = 7.8 Hz, 2H), 2.43 (s, 3H), 3.63 (ddd, ^3J = ^3J = 7.8 Hz, ^3J = 1.8 Hz, 1H), 4.08 (d, ^3J = 1.8 Hz, 1H), 5.51 (s, 2H), 7.32 (d, ^3J = 8.3 Hz, 2H), 7.40−7.55 (m, 3H), 7.69 (d, ^3J = 8.3 Hz, 2H), 7.78 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q), 17.3 (q), 21.2 (s), 31.6 (t), 43.0 (d), 56.6 (d), 64.0 (s), 96.8 (s), 97.8 (s), 127.1 (d), 127.2 (d), 127.5 (d), 128.3 (d), 128.7 (d), 129.0 (d), 132.7 (s), 133.1 (d), 135.9 (s), 137.4 (s).

Isomer 9d′. ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3H), 1.01 (s, 3H), 2.23 (d, ^3J = 7.4 Hz, 2H), 2.43 (s, 3H), 3.67 (ddd, ^3J = ^3J = 7.4 Hz, ^3J = 1.8 Hz, 1H), 4.12 (d, ^3J = 1.8 Hz, 1H), 5.51 (s, 2H), 7.31 (d, ^3J = 8.3 Hz, 2H), 7.40−7.55 (m, 3H), 7.67 (d, ^3J = 8.3 Hz, 2H), 7.80 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q), 17.3 (q), 21.2 (s), 31.6 (t), 43.0 (d), 56.6 (d), 64.0 (s), 96.7 (s), 97.9 (s), 127.1 (d), 127.1 (d), 127.6 (d), 128.3 (d), 128.8 (d), 129.0 (d), 132.7 (s), 133.4 (d), 135.9 (s), 137.5 (s).

(1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-1-(4′-chlorophenyl)-8,8-dimethyl-4-phenyl- [9e, X = *p*-Cl, Y = H] and (1a,4a,-4aα,7aα)-4,4a,7,7a-Tetrahydro-4-(4′-chlorophenyl)-8,8-dimethyl-1-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine [9e′, X = H, Y = *p*-Cl]: 42%, colorless needles, mp 149−150 °C dec, R_f = 0.18 (silica gel, 3:2 methylene chloride:petroleum ether). IR (KBr): ν = 3020 cm^{-1}, 2940, 2900, 1575, 1480, 1450, 1360, 1290, 1080, 1000, 810, 750, 720, 695. UV (benzene): λ_{max} (ϵ) 328 nm (sh, 26), 350 (sh, 93), 361 (173). Anal. Calcd for $C_{22}H_{21}N_2Cl$ (348.9): C, 75.74; H, 6.07; N, 8.03. Found: C, 75.29; H, 6.04; N, 7.70.

Isomer 9e. ^{1}H NMR: δ = 0.19 (s, 3H), 1.01 (s, 3H), 2.21 (d, ^3J = 8.5 Hz, 2H), 3.60 (ddd, ^3J = ^3J = 8.5 Hz, ^3J = 6.3 Hz, 1H), 4.06 (d, ^3J = 6.3 Hz, 1H), 5.50 (s, 2H), 7.41−7.55 (m, 3H), 7.47 (d, ^3J = 8.6 Hz, 2H), 7.75 (d, ^3J = 8.6 Hz, 2H), 7.77 (dd, ^3J = 8.0 Hz, ^4J = 1.7 Hz, 2H). ^{13}C NMR: δ = 16.9 (q), 17.2 (q), 31.5 (t), 43.0 (d), 56.8 (d), 64.1 (s), 97.0 (s), 97.3 (s), 127.0 (d), 127.1 (d), 127.9 (d), 128.4 (d), 128.6 (d), 128.9 (d), 133.4 (d), 133.7 (s), 134.3 (s), 135.4 (s).

Isomer 9e′. ^{1}H NMR: δ = 0.19 (s, 3H), 1.01 (s, 3H), 2.21 (d, ^3J = 8.3 Hz, 2H), 3.60 (ddd, ^3J = ^3J = 8.3 Hz, ^3J = 6.8 Hz, 1H), 4.12 (d, ^3J = 6.8 Hz, 1H), 5.50 (s, 2H), 7.41−7.55 (m, 3H), 7.48 (d, ^3J = 8.5 Hz, 2H), 7.73 (d, ^3J = 8.5 Hz, 2H), 7.78 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 2H). ^{13}C NMR: δ = 16.9 (q), 17.3 (q), 31.5 (t), 43.2 (d), 56.6 (d), 64.1 (s), 96.2 (s), 98.0 (s), 126.7 (d), 127.5 (d), 127.8 (d), 128.4 (s), 128.5 (d), 128.6 (d), 133.8 (s), 133.8 (d), 134.4 (s), 135.5 (s).

(1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-1-(4′-carbomethoxyphenyl)-8,8-dimethyl-4-phenyl- [9g, X = *p*-CO$_2$Me, Y = H] and (1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-4-(4′-carbomethoxyphenyl)-8,8-dimethyl-1-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [9g′, X = H, Y = *p*-CO$_2$Me]: 75%, colorless needles, mp 129−130 °C dec, R_f = 0.33 (silica gel, 33:1 methylene chloride:*tert*-butyl methyl ether). IR (KBr): ν = 3020 cm^{-1}, 2940, 2890, 1700, 1595, 1420, 1270, 1190, 1100, 1005, 840, 690. UV (benzene): λ_{max} (ϵ) 329 nm (sh, 34), 349 (sh, 100), 360 (175). Anal. Calcd for $C_{24}H_{24}N_2O_2$ (372.5): C, 77.39; H, 6.49; N, 7.52. Found: C, 77.32; H, 6.16; N, 7.09.

Isomer 9g. ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3H), 1.02 (s, 3H), 2.14−2.19 (m, 2H), 3.57−3.73 (m, 1H), 3.94 (s, 3H), 4.08−4.16 (m, 1H), 5.43−5.53 (m, 2H), 7.40−7.54 (m, 3H), 7.76 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2H), 7.89 (d, ^3J = 8.6 Hz, 2H), 8.17 (d, ^3J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.3 (q), 31.5 (t), 43.3 (d), 52.1 (q), 56.9 (d), 64.4 (s), 96.5 (s), 97.5 (s), 127.0 (d), 127.1 (d), 127.5 (d), 127.9 (d), 128.4 (d), 129.6 (s), 129.6 (d), 133.4 (d), 135.3 (s), 141.0 (s), 166.8 (s).

Isomer 9g′. ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3H), 1.02 (s, 3H), 2.14−2.19 (m, 2H), 3.57−3.73 (m, 1H), 3.94 (s, 3H), 4.08−4.16 (m, 1H), 5.43−5.53 (m, 2H), 7.40−7.54 (m, 3H), 7.78 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2H), 7.87 (d, ^3J = 8.6 Hz, 2H), 8.16 (d, ^3J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.3 (q), 31.5 (t), 43.0 (d), 52.1 (q), 56.6 (d), 64.4 (s), 97.1 (s), 98.2 (s), 126.7 (d), 127.1 (d), 127.5 (d), 127.9 (d), 128.4 (d), 129.6 (s), 129.6 (d), 133.7 (d), 135.3 (s), 141.1 (s), 166.8 (s).

(1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-1-(4′-cyanophenyl)-8,8-dimethyl-4-phenyl- [9h, X = *p* -CN, Y = H] and (1a,-4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-4-(4′-cyanophenyl)-8,8-dimethyl-1-phenyl-1,4-methano-1*H*-cyclopenta[*d*]-pyridazine [9h′, X = H, Y = *p*-CN]: 84%, colorless needles, mp 160−161 °C dec, R_f = 0.12 (silica gel, methylene chloride). IR (KBr): ν = 3040 cm^{-1}, 2960, 2930, 2210, 1595, 1490, 1455, 1365, 1010, 820, 760, 740, 730, 700. UV (benzene): λ_{max} (ϵ) 329 nm (sh, 33), 350 (sh, 101), 360 (177). Anal. Calcd for $C_{23}H_{21}N_3$ (339.4): C, 81.39; H, 6.24; N, 12.38. Found: C, 81.46; H, 6.45; N, 11.92.

Isomer 9h. ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3H), 1.03 (s, 3H), 2.15−2.26 (m, 2H), 3.69 (ddd, ^3J = ^3J = 8.6 Hz, ^3J = 6.4 Hz, 1H), 4.03−4.17 (m, 1H), 5.50 (s, 2H), 7.39−7.55 (m, 3H), 7.74 (dd, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 2H), 7.80 (d, ^3J = 8.7 Hz, 2H), 7.94 (d, ^3J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.3 (q), 31.4 (t), 43.4 (d), 57.0 (d), 64.6 (s), 96.1 (s), 97.4 (s), 111.7 (s), 118.7 (s), 127.0 (d), 127.1 (d), 128.0 (d), 128.2 (d), 128.5 (d), 132.2 (d), 133.4 (d), 135.0 (s), 141.4 (s).

Isomer 9h′. ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 3H), 1.03 (s, 3H), 2.15−2.26 (m, 2H), 3.62 (ddd, ^3J = 9.2 Hz, ^3J = 8.6 Hz, ^3J = 5.3 Hz, 1H), 4.03−4.17 (m, 1H), 5.43 (ddd, ^3J = 5.8 Hz, ^3J = 4.3 Hz, ^4J = 2.2 Hz, 1H), 5.50 (ddd, ^3J = 5.9 Hz, ^3J = 4.2 Hz, ^3J = 2.2 Hz, 1H), 7.39−7.55 (m, 3H), 7.76 (dd, ^3J = 6.6 Hz, ^4J = 1.4 Hz, 2H), 7.79 (d, ^3J = 8.7 Hz, 2H), 7.92 (d, ^3J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.3 (q), 31.5 (t), 43.1 (d), 56.7 (d), 64.6 (s), 97.1 (s), 98.5 (s), 111.8 (s), 118.7 (s), 126.3 (d), 127.5 (d), 127.9 (d), 128.1 (d), 128.5 (d), 132.2 (d), 134.3 (d), 135.0 (s), 141.5 (s).

(1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-(4′-nitrophenyl)-4-phenyl- [9i, X = *p* -NO$_2$, Y = H] and (1a,4a,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1-phenyl-4-(4′-nitrophenyl)-1,4-methano-1*H*-cyclopenta[*d*]pyridazine [9i′, X = H, Y = *p*-NO$_2$]: 57%, colorless needles, mp 162−163 °C dec, R_f = 0.21 (silica gel, methylene chloride). IR (KBr): ν = 3020 cm^{-1}, 2940, 2890, 2820, 1580, 1505, 1480, 1340, 1310, 1285, 1090, 1005, 690. UV (benzene): λ_{max} (ϵ) 360 (sh, 440). Anal. Calcd for $C_{22}H_{21}N_3O_2$ (359.4): C, 73.52; H, 5.89; N, 11.69. Found; C, 73.78; H, 5.85; N, 11.26.

Isomer 9i. ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H), 1.06 (s, 3H), 2.16−2.27 (m, 2H), 3.65 (ddd, ^3J = ^3J = 8.6 Hz, ^3J = 5.2 Hz, 1H), 4.14−4.21 (m, 1H), 5.51 (s, 2H), 7.42−7.56 (m, 3H), 7.75 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 2H), 8.01 (d, ^3J = 8.9 Hz, 2H), 8.37 (d, ^3J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q), 17.3 (q), 31.4 (t), 43.6 (d), 56.7 (d), 64.6 (s), 97.0 (s), 97.4 (s), 123.6 (d), 126.9 (d), 127.1 (d), 128.1 (d), 128.4 (d), 128.4 (d), 133.3 (d), 134.9 (s), 143.5 (s), 147.7 (s).

Isomer 9i′. ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H), 1.00 (s, 3H), 2.16−2.27 (m, 2H), 3.70 (ddd, ^3J = ^3J = 8.4 Hz, ^3J = 6.3 Hz, 1H), 4.06−4.16 (m, 1H), 5.44 (ddd, ^3J = 5.8 Hz, ^3J = 4.4 Hz, ^4J = 2.2 Hz, 1H), 5.55 (ddd, ^3J = 5.8 Hz, ^3J = 4.2 Hz, ^3J = 2.1 Hz, 1H), 7.42−7.56 (m, 3H), 7.77 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 2H), 7.99 (d, ^3J = 9.0 Hz, 2H), 8.36 (d, ^3J = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.8 (q), 17.3 (q), 31.5 (t), 43.1 (d), 57.2 (d), 64.6 (s), 96.0 (s), 98.5 (s), 123.6 (d), 126.2 (d), 127.5 (d), 128.0 (d), 128.3 (d), 128.4 (d), 134.3 (d), 134.9 (s), 143.5 (s), 147.5 (s).

General Hydrogenation Procedure for the Azoalkanes 10. (i) Azoalkanes 10c−e,g−i. To a solution of 1.50 mmol of azoalkane **9c−e,g−i** in 6.0 mL of methanol and 14 mL of methylene chloride were added 5.00 g of dipotassium azodicarboxylate.[18] After addition of 0.5 mL of acetic acid, the reaction mixture was stirred for 4 d at ambient temperature (ca. 20 °C) and 20 mL of 0.5 N NaOH was added. The product was isolated by extraction with methylene chloride (3 × 15 mL), and the organic layer was dried over a mixture of magnesium sulfate and potassium carbonate. The solvent was removed by distillation (ca. 20 °C, 20 Torr), and the crude product was purified by column chromatography. **(ii) Azoalkane 10f.** To a solution of 1.50 mmol of azoalkane **9i** in 85 mL of ethyl acetate and 45 mL of ethanol was added a catalytic amount of palladium (on charcoal), and the mixture was stirred for 8 h under a hydrogen gas atmosphere. The catalyst was removed by filtration and the solvent by distillation (ca. 20 °C, 20 Torr), and the crude product was purified by column chromatography.

(18) Berson, J. A.; Poonian, M. S.; Libbey, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 5567.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(4′-methoxyphenyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10c, X = *p*-MeO): 92%, colorless needles, mp 157−158 °C dec, R_f = 0.20 (silica gel, methylene chloride). IR (KBr): ν = 3030 cm^{-1}, 2940, 1600, 1510, 1440, 1295, 1245, 1180, 1020, 810, 750, 700. UV (benzene): λ_{max} (ϵ) = 330 nm (sh, 24), 352 (sh, 75), 363 (113). ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 3H), 0.95 (s, 3H), 1.37−1.67 (m, 6H), 3.44−3.55 (m, 2H), 3.86 (s, 3H), 7.02 (d, ^3J = 9.7 Hz, 2H), 7.15−7.52 (m, 3H), 7.67 (d, ^3J = 9.7 Hz, 2H), 7.75 (dd, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q), 17.8 (q), 25.5 (t), 25.5 (t), 28.5 (t), 48.8 (d), 48.8 (d), 55.2 (q), 66.0 (s), 98.2 (s), 98.2 (s), 113.7 (d), 127.4 (d), 127.6 (d), 128.3 (d), 128.3 (d), 128.6 (d), 136.3 (s), 159.1 (s). Anal. Calcd for $C_{23}H_{26}N_2O$ (346.5): C, 79.73; H, 7.56; N, 8.09. Found: C, 79.29; H, 7.18; N, 7.74.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(4′-methylphenyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10d, X = *p*-Me): 92%, colorless needles, mp 147−148 °C dec, R_f = 0.34 (silica gel, methylene chloride). IR (KBr): ν = 3010 cm^{-1}, 2940, 1480, 1455, 1430, 1290, 1015, 795, 755, 690. UV (benzene): λ_{max} (ϵ) = 330 nm (sh, 22), 352 (sh, 77), 363 (118). ^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 3H), 0.97 (s, 3H), 1.45−1.63 (m, 6H), 2.42 (s, 3H), 3.48−3.54 (m, 2H), 7.20 (d, ^3J = 8.0 Hz, 2H), 7.44 (tt, ^3J = 9.4 Hz, ^3J = 8.2 Hz, 2H), 7.47 (tt, ^3J = 9.4 Hz, ^4J = 1.6 Hz, 1H), 7.64 (d, ^3J = 8.0 Hz, 2H), 7.76 (dd, ^3J = 8.2 Hz, ^4J = 1.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 17.0 (q), 17.8 (q), 21.2 (s), 25.5 (t), 25.5 (t), 28.6 (t), 48.8 (d), 48.8 (d), 66.0 (s), 98.3 (s), 98.3 (s), 127.4 (d), 127.5 (d), 127.6 (d), 128.3 (d), 129.0 (d), 133.2 (s), 136.3 (s), 137.3 (s). Anal. Calcd for $C_{23}H_{26}N_2$ (330.5): C, 83.59; H, 7.93; N, 8.48. Found: C, 83.26; H, 7.61; N, 8.11.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(4′-chlorophenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10e, X = *p*-Cl): 80%, colorless needles, mp 137 −138 °C dec, R_f = 0.52 (silica gel, methylene chloride). IR (KBr): ν = 3040 cm^{-1}, 2940, 1485, 1460, 1435, 1090, 1010, 810, 745, 700. UV (benzene): λ_{max} (ϵ) = 329 nm (sh, 23), 351 (sh, 73), 362 (115). ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 3H), 0.97 (s, 3H), 1.41−1.63 (m, 6H), 3.40−3.59 (m, 2H), 7.39−7.53 (m, 3H), 7.45 (d, ^3J = 8.6 Hz, 2H), 7.70 (d, ^3J = 8.6 Hz, 2H), 7.74 (dd, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.8 (q), 25.4 (t), 25.4 (t), 28.5 (t), 48.8 (d), 49.0 (d), 66.2 (s), 97.7 (s), 98.5 (s), 127.5 (d), 127.8 (d), 128.3 (d), 128.6 (d), 128.8 (d), 133.6 (s), 134.8 (s), 135.9 (s). Anal. Calcd for $C_{22}H_{23}ClN_2$ (350.9): C, 75.31; H, 6.61; N, 7.98. Found: C, 74.95; H, 7.06; N, 7.56.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(4′-aminophenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10f, X = *p*-NH$_2$): 20%, colorless needles; mp 73−74 °C dec, R_f = 0.48 (silica gel, 9:1 methylene chloride: *tert*-butyl methyl ether). IR (KBr): ν = 3440 cm^{-1}, 3340, 3020, 2940, 1610, 1510, 1460, 1295, 1180, 700. UV (benzene): λ_{max} (ϵ) = 352 nm (sh, 74), 364 (105). ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 3H), 0.93 (s, 3H), 1.38−1.58 (m, 6H), 3.39−3.52 (m, 2H), 3.70 (b s, 2H), 6.79 (d, ^3J = 8.6 Hz, 2H), 7.34−7.52 (m, 3H), 7.51 (d, ^3J = 8.6 Hz, 2H), 7.74 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.8 (q), 25.5 (t), 25.5 (t), 28.5 (t), 48.6 (d), 48.8 (d), 65.9 (s), 98.0 (s), 98.4 (s), 114.9 (d), 126.1 (s), 127.4 (d), 127.6 (d), 128.3 (d), 128.5 (d), 136.5 (s), 145.9 (s). Anal. Calcd for $C_{22}H_{25}N_3$ (331.5): C, 79.72; H, 7.60; N, 12.68. Found: C, 79.51; H, 7.70; N, 12.46.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(4′-carbomethoxyphenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10g, X = *p*-CO$_2$Me): 85%, colorless needles, mp 132 −133 °C dec, R_f = 0.28 (silica gel, methylene chloride). IR (KBr): ν = 3040 cm^{-1}, 2930, 1710, 1600, 1445, 1275, 1190, 1105, 1015, 750, 690. UV (benzene): λ_{max} (ϵ) = 330 nm (sh, 41), 350 (sh, 78), 362 (111). ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 3H), 0.99 (s, 3H), 1.42−1.62 (m, 6H), 3.51−3.57 (m, 2H), 3.94 (s, 3H), 7.36−7.53 (m, 3H), 7.75 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 2H), 7.85 (d, ^3J = 8.4 Hz, 2H), 8.15 (d, ^3J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.8 (q), 25.4 (t), 25.4 (t), 28.5 (t), 48.8 (d), 49.1 (d), 52.1 (q), 66.5 (s), 98.0 (s), 98.7 (s), 127.4 (d), 127.4 (d), 127.8 (d), 128.3 (d), 129.5 (s), 129.6 (d), 135.7 (s), 141.2 (s), 166.9 (s). Anal. Calcd for $C_{24}H_{26}N_2O_2$ (374.5): C, 76.98; H; 7.00; N, 7.48. Found: C, 77.08; H, 6.71; N, 7.16.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-1-(4′-cyanophenyl)-8,8-dimethyl-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10h, X = *p*-CN): 80%, cololess needles, mp 147−149 °C dec, R_f = 0.17 (silica gel, methylene chloride). IR (KBr): ν = 3030 cm^{-1}, 2930, 2840, 2210, 1590, 1490, 1450, 1430, 1360, 1010, 650, 600. UV (benzene): λ_{max} (ϵ) 330 nm (sh, 25), 351 (sh, 78), 362 (119). ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 3H), 1.00 (s, 3H), 1.41−1.62 (m, 6H), 3.43−3.63 (m, 2H), 7.36−7.54 (m, 3H), 7.73 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H), 7.78 (d, ^3J = 8.6 Hz, 2H), 7.90 (d, ^3J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.8 (q), 25.4 (t), 25.4 (t), 28.5 (t), 48.9 (d), 49.2 (d), 66.6 (s), 97.6 (s), 98.9 (s), 111.6 (s), 118.8 (s), 127.4 (d), 128.0 (d), 128.1 (d), 128.4 (d), 132.2 (s), 135.4 (s), 141.8 (s). Anal. Calcd for $C_{23}H_{23}N_3$ (341.5): C, 80.90; H, 6.79; N, 12.31. Found: C, 80.62; H, 7.00; N, 12.15.

(1a,4a,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1-(4′-nitrophenyl)-4-phenyl-1,4-methano-1*H*-cyclopenta[*d*]pyridazine (10i, X = *p*-NO$_2$): 90%, colorless needles, mp 144−145 °C dec, R_f = 0.48 (silica gel, methylene chloride). IR (KBr): ν = 3040 cm^{-1}, 2940, 1590, 1510, 1460, 1440, 1340, 850, 740, 690. UV (benzene): λ_{max} (ϵ) 360 nm (sh, 360). ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 3H), 1.03 (s, 3H), 1.41−1.62 (m, 6H), 3.46−3.64 (m, 2H), 7.37−7.54 (m, 3H), 7.73 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2H), 7.97 (d, ^3J = 8.9 Hz, 2H), 8.35 (d, ^3J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 16.9 (q), 17.9 (q), 25.4 (t), 25.4 (t), 28.5 (t), 48.9 (d), 49.5 (d), 66.7 (s), 97.5 (s), 99.0 (s), 123.6 (d), 127.5 (d), 128.0 (d), 128.3 (d), 128.4 (d), 135.4 (s), 143.9 (s), 147.5 (s). Anal. Calcd for $C_{22}H_{23}N_3O_2$ (361.4): C, 73.11; H, 6.41; N, 11.63. Found: C, 72.70; H, 6.37; N, 11.15.

General Procedure for the Preparation of Housanes 11. The housanes were synthesized in analogy to literature procedure.[5] The derivatives **11a**,**c**−**e**,**g**,**h** were obtained by direct irradiation with a CW argon ion laser (widened beam) and **11f**,**i** by thermolysis in refluxing toluene of the corresponding azoalkanes **10**.

3,3-Dimethyl-2,4-diphenyl-*endo*-tricyclo[3.3.0.0^{2,4}]-octane (11a, X = H): 99%, colorless oil, R_f = 0.94 (silica gel, methylene chloride). IR (film): ν = 3140 cm^{-1}, 3110, 2920, 2840, 1590, 1480, 1450, 1435, 1070, 1020, 770, 755, 725, 700. ^{1}H NMR ($CDCl_3$): δ = 0.64 (s, 3H), 1.50 (s, 3H), 1.30−1.70 and 1.88−2.10 (m, 6H), 2.66 (d, ^3J = 6.0 Hz, 2H), 7.20−7.36 (m, 10H). ^{13}C NMR ($CDCl_3$): δ = 14.6 (q), 23.1 (q), 25.1 (t), 28.3 (t), 29.6 (s), 43.4 (d), 44.8 (s), 125.6 (d), 127.7 (d), 129.9 (d), 138.5 (s). Anal. Calcd for $C_{22}H_{24}$ (288.4): C, 91.61; H, 8.39. Found: C, 91.72; H, 8.08.

3,3-Dimethyl-2-(4′-methoxyphenyl)-4-phenyl-*endo*-tricyclo[3.3.0.0^{2,4}]octane (11c, X = *p*-MeO): 95%, colorless oil, R_f = 0.88 (silica gel, methylene chloride). IR (film): ν = 3030 cm^{-1}, 3000, 2920, 2840, 1590, 1500, 1445, 1430, 1235, 1165, 1035, 1020, 820, 700. ^{1}H NMR ($CDCl_3$): δ = 0.63 (s, 3H), 1.48 (s, 3H), 1.34−1.71 and 1.88−2.10 (m, 6H), 2.59 (dd, ^3J = 6.5 Hz, ^3J = 4.1 Hz, 1H), 2.65 (dd, ^3J = 6.1 Hz, ^3J = 4.1 Hz, 1H), 3.81 (s, 3H), 6.86 (d, ^3J = 8.9 Hz, 2H), 7.19 (d, ^3J = 8.9 Hz, 2H), 7.16−7.33 (m, 5H). ^{13}C NMR ($CDCl_3$): δ = 14.6 (q), 23.2 (q), 25.1 (t), 28.3 (t), 28.3 (t), 29.4 (s), 43.2 (d), 43.3 (d), 44.1 (s), 44.5 (s), 55.1 (q), 113.2 (d), 125.4 (d), 127.6 (d), 129.7 (d), 130.3 (s), 131.0 (d), 138.7 (s), 157.6 (s). Anal. Calcd for $C_{23}H_{26}O$ (318.5): C, 86.75; H, 8.23. Found: C, 86.57; H, 8.38.

3,3-Dimethyl-2-(4′-methylphenyl)-4-phenyl-*endo*-tricyclo[3.3.0.0^{2,4}]octane (11d, X = *p*-Me): 95%, colorless oil, R_f = 0.93 (silica gel, methylene chloride). IR (film): ν = 3030 cm^{-1}, 3000, 2940, 2840, 1585, 1500, 1480, 1430, 800, 700. ^{1}H NMR ($CDCl_3$): δ = 0.63 (s, 3H), 1.48 (s, 3H), 1.34−1.70 and 1.88−2.13 (m, 6H), 2.34 (s, 3H), 2.61 (dd, ^3J = 6.0 Hz, ^3J = 4.0 Hz, 1H), 2.65 (dd, ^3J = 6.0 Hz, ^3J = 4.0 Hz, 1H), 7.09−7.36 (m, 9H). ^{13}C NMR ($CDCl_3$): δ = 14.7 (q), 21.1 (q), 23.0 (q), 25.1 (t), 28.3 (t), 28.3 (t), 29.5 (s), 43.3 (d), 43.4 (d), 44.4 (s), 44.6 (s), 125.5 (d), 127.6 (d), 128.4 (d), 129.8 (d), 129.9 (d), 135.1 (s), 135.2 (s), 138.7 (s). Anal. Calcd for $C_{23}H_{26}$ (302.5): C, 91.34; H, 8.66. Found: C, 91.28; H, 8.64.

2-(4′-Chlorophenyl)-3,3-dimethyl-4-phenyl-*endo*-tricyclo[3.3.0.0^{2,4}]octane (11e, X = *p*-Cl): 95%, colorless oil, R_f = 0.96 (silica gel, methylene chloride). IR (film): ν = 3030

cm^{-1}, 3000, 2920, 2840, 1585, 1475, 1080, 1005, 810, 725, 700. ^{1}H NMR ($CDCl_3$): δ = 0.62 (s, 3H), 1.48 (s, 3H), 1.31−1.72 and 1.84−2.09 (m, 6H), 2.64 (d, ^3J = 6.2 Hz, 2H), 7.17−7.35 (m, 5H), 7.16 (d ^3J = 8.7 Hz, 2H), 7.27 (d, ^3J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 14.6 (q), 23.0 (q), 25.1 (t), 28.2 (t), 28.2 (t), 29.7 (s), 43.2 (d), 43.4 (d), 44.1 (s), 44.9 (s), 125.8 (d), 127.8 (d), 127.9 (d), 129.8 (d), 131.1 (d), 131.3 (s), 137.1 (s), 138.1 (s). Anal. Calcd for $C_{22}H_{23}Cl$ (322.9): C, 81.84; H, 7.18. Found: C, 81.85; H, 6.98.

2-(4′-Aminophenyl)-3,3-dimethyl-4-phenyl-*endo*-tricyclo-[3.3.0.0^{2,4}]octane (11f, X = *p*-NH$_2$): 80%, colorless oil, R_f = 0.88 (silica gel, methylene chloride). IR (film): ν = 3420 cm^{-1}, 3340, 3000, 2910, 1600, 1500, 1430, 1330, 1260, 1170, 900, 815, 715, 700. ^{1}H NMR ($CDCl_3$): δ = 0.63 (s, 3H), 1.46 (s, 3H), 1.34−1.68 and 1.86−2.11 (m, 6H), 2.56 (dd, ^3J = 6.7 Hz, ^3J = 4.0 Hz, 1H), 2.64 (dd, ^3J = 6.6 Hz, ^3J = 4.0 Hz, 1H), 6.66 (d, ^3J = 8.5 Hz, 2H), 7.07 (d, ^3J = 8.5 Hz, 2H), 7.16−7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): δ = 14.6 (q), 23.1 (q), 25.1 (t), 28.3 (t), 28.4 (t), 29.3 (s), 43.1 (d), 43.4 (d), 44.1 (s), 44.4 (s), 114.7 (d), 122.9 (s), 125.3 (d), 127.5 (d), 129.7 (d), 131.0 (d), 139.0 (s), 144.1 (s). Anal. Calcd for $C_{22}H_{25}N$ (303.4): C, 87.08; H, 8.30; N, 4.62. Found: C, 86.81; H, 8.51; N, 4.55.

2-(4′-Carbomethoxyphenyl)-3,3-dimethyl-4-phenyl-*endo*-tricyclo[3.3.0.0^{2,4}]octane (11g, X = *p*-CO$_2$Me): 90%, colorless oil, R_f = 0.61 (silica gel, methylene chloride). IR (film): ν = 3030 cm^{-1}, 3000, 2920, 2830, 1705, 1590, 1420, 1265, 1100, 700. ^{1}H NMR ($CDCl_3$): δ = 0.63 (s, 3H), 1.50 (s, 3H), 1.37−1.72 and 1.82−2.06 (m, 6H), 2.65 (dd, ^3J = 6.5 Hz, ^3J = 4.1 Hz, 1H), 2.71 (dd, ^3J = 6.2 Hz, ^3J = 4.1 Hz, 1H), 3.90 (s, 3H), 7.19−7.36 (m, 5H), 7.28 (d, ^3J = 8.6 Hz, 2H), 7.97 (d, ^3J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 14.7 (q), 22.9 (q), 25.0 (t), 28.2 (t), 28.2 (t), 30.4 (s), 43.3 (d), 43.5 (d), 44.7 (s), 45.5 (s), 51.9 (q), 126.0 (d), 127.3 (s), 127.8 (d), 128.9 (d), 129.7 (d), 130.0 (d), 137.7 (s), 144.7 (s), 167.2 (s). Anal. Calcd for $C_{24}H_{26}O_2$ (346.5): C, 83.20; H, 7.56. Found: C, 83.00; H, 7.76.

2-(4′-Cyanophenyl)-3,3-dimethyl-4-phenyl-*endo*-tricyclo-[3.3.0.0^{2,4}]octane (11h, X = *p*-CN): 92%, colorless oil, R_f = 0.29 (silica gel, 20:1 petroleum ether:ethyl acetate). IR (film): ν = 3030 cm^{-1}, 3000, 2920, 2830, 2210, 1585, 1480, 1430, 835, 820, 740, 700. ^{1}H NMR ($CDCl_3$): δ = 0.64 (s, 3H), 1.52 (s, 3H), 1.37−1.75 and 1.82−2.07 (m, 6H), 2.66 (dd, ^3J = 6.5 Hz, ^3J = 4.1 Hz, 1H), 2.74 (dd, ^3J = 6.5 Hz, ^3J = 4.1 Hz, 1H), 7.21−7.39 (m, 5H), 7.30 (d, ^3J = 8.6 Hz, 2H), 7.57 (d, ^3J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 14.7 (q), 22.8 (q), 25.0 (t), 28.0 (t), 28.1 (t), 30.8 (s), 43.0 (d), 43.5 (d), 44.5 (s), 45.8 (s), 109.0 (s), 119.2 (s), 126.2 (d), 127.9 (d), 129.9 (d), 130.0 (d), 131.3 (d), 137.2 (s), 145.0 (s). Anal. Calcd for $C_{23}H_{23}N$ (313.4): C, 88.14; H, 7.40; N, 4.47. Found: C, 87.91; H, 7.32; N, 4.20.

3,3-Dimethyl-2-(4′-nitrophenyl)-4-phenyl-*endo*-tricyclo-[3.3.0.0^{2,4}]octane (11i, X = *p*-NO$_2$): 95%, colorless needles, mp 115−117 °C, R_f = 0.94 (silica gel, methylene chloride). IR (KBr): ν = 2920 cm^{-1}, 2880, 2840, 1580, 1495, 1430, 1130, 1100, 835, 705. ^{1}H NMR ($CDCl_3$): δ = 0.64 (s, 3H), 1.51 (s, 3H), 1.36−1.74 and 1.79−2.05 (m, 6H), 2.64 (dd, ^3J = 6.4 Hz, ^3J = 4.0 Hz, 1H), 2.75 (dd, ^3J = 6.4 Hz, ^3J = 4.0 Hz, 1H), 7.21−7.38 (m, 5H), 7.31 (d, ^3J = 8.3 Hz, 2H), 8.23 (d, ^3J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 14.8 (q), 22.8 (q), 25.0 (t), 28.1 (t), 28.2 (t), 31.3 (s), 43.2 (d), 43.7 (d), 44.6 (s), 46.2 (s), 122.9 (d), 126.3 (d), 128.1 (d), 130.0 (d), 130.1 (d), 133.6 (s), 137.1 (s), 147.7 (s). Anal. Calcd for $C_{22}H_{23}NO_2$ (333.4): C, 79.25; H, 6.95; N, 4.20. Found: C, 78.96; H, 7.09; N, 4.01.

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Note added in proof: In the customary coordinate system, in which the *D* and *E* parameters of planar π systems are represented, the *z* axis is chosen parallel to the *p* orbitals (eq 3 and eq 4). However, for localized diradicals it is more apporpriate to define the *z* axis along the line which connects the two radical sites. In this case the relation $D \geq 3E \geq 0$ is fulfilled and allows a quantitative comparison of the theoretical with the experimental zero-field splitting parameters. This coordinate transformation requires multiplication of the expressions in eq 4 and eq 6 by a distance dependent factor (in the present case f(2.4 Å) = 1.5); its analytical expression is given in Gouterman M.; Moffitt W. *J. Chem. Phys.* **1959**, *30*, 1107.

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