Electronic substituent effects on the EPR-spectral *D* parameter of trimethylenemethane (TMM) triplet diradicals compared with localized cyclopentane-1,3-diyls

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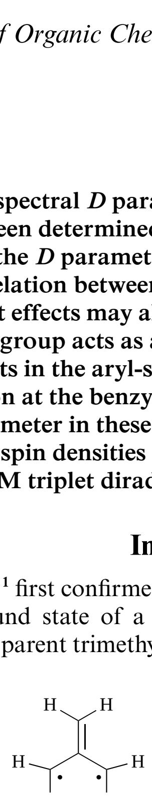
The EPR-spectral *D* parameter for a series of aryl-substituted trimethylenemethane (TMM) derivatives 2a–g has been determined in a 2-methyltetrahydrofuran (MTHF) matrix at 77 K. Although the substituent effects on the *D* parameter are relatively small compared with those of the localized 1,3-diradicals 4, the good correlation between the *D* values of TMMs 2 and those established for 4 signifies that electronic substituent effects may also be adequately monitored in this way for cross-conjugated triplet species. Thus, the *p*-NO_2 group acts as a spin acceptor, while the *p*-F substituent behaves as a spin donor. Significant steric effects in the aryl-substituted TMMs 2a–m impose a twisted conformation and, thus, reduce conjugation at the benzyl-radical center and are responsible for the relatively small substituent effects on the *D* parameter in these TMM triplets. Moreover, good linearity is observed between the AM1/AUHF-calculated spin densities at the benzyl position for the twisted conformation and the experimental *D* values of the TMM triplet diradicals 2.

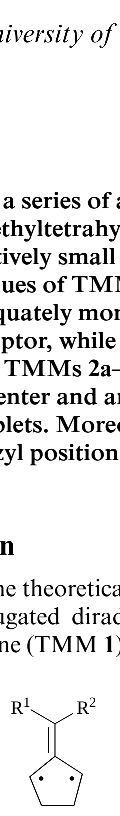
Introduction

Paul Dowd[1] first confirmed in 1966 the theoretically predicted[2] triplet ground state of a cross-conjugated diradical species,[†] namely the parent trimethylenemethane (TMM **1**), by means of EPR spectroscopy under matrix isolation. A major contribution in this area was achieved by Berson and co-workers,[4] who devised a convenient synthesis of the cyclic TMM derivatives **2**, which enabled them to explore in detail the chemical and physical properties of these unusual diradicals.[5]



1

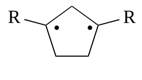
D/cm^{-1} 0.024



2

0.0265

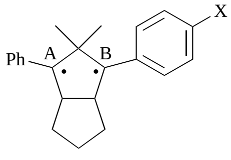
($R^1 = R^2 = H$)



3

0.084 (R = H)

0.045 (R = Ph)



4

0.0506 (X = H)

Another class of related cyclic diradicals are the localized ones, of which the parent species **3** was reported by Closs[6] in 1975, the triplet ground state of which was again established by EPR measurements at 4 K. Through the facile Hünig isopyrazole route[7] for the preparation of the azoalkanes as precursors, a large variety of aryl-substituted derivatives of the bicyclic type **4** was made available by us, to assess electronic substituent effects in such localized triplet diradicals through the EPR-spectral *D* parameter.[8] Theoretical consideration[8b] provided a simple functional relationship for these localized triplet diradicals between the experimental *D* value and the theoretical spin densities ρ_A and ρ_B (readily computed by semiempirical calculations) at the radical centers A and B, separated by the interradical distance d_{AB} [eqn. (1)]. Indeed, an

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

excellent ($r^2 = 0.963$) linear correlation between the *D* value and the spin density (ρ) at the cumyl radical site was demonstrated for a large number of substituents.[8e] For the first time electronic effects such as spin delocalization and radical stabilization in benzyl-type radicals could be quantitatively described in terms of the EPR-spectral *D* parameter of triplet diradicals; in fact, a good correspondence with the chemical σ_{rad} scales[9] was shown to apply.[8e]

The question arises as to whether electronic effects in radicals may be sensed through appropriately substituted Berson-type TMM triplet diradicals **2**. A few substituted derivatives of **2** ($R^1 = H$, $R^2 = Ar$) have been reported,[4a] but no clear-cut correlation between the *D* values and the electronic character of the examined substituents was discernible. Consequently, we decided to cover the full range of substituents in the TMMs **2** ($R^1 = H$, $R^2 = Ar$) from *p*-NH_2 to *p*-NO_2, in order to assess whether in these cross-conjugated triplet diradicals electronic substituent effects parallel those established for the localized ones of the cyclopentane-1,3-diyl type **4**.[‡] Herein we report the results of our study.

Results and discussion

The diazenes **5**, the precursors of the TMM derivatives **2**, were synthesized by analogy to the reported methods (Scheme 1).[4a] The fulvenes **8**, prepared according to the literature,[11,12] were converted into the corresponding [4 + 2] cycloadducts **7** with ethyl azodicarboxylate (DEAD) and reduced catalytically to

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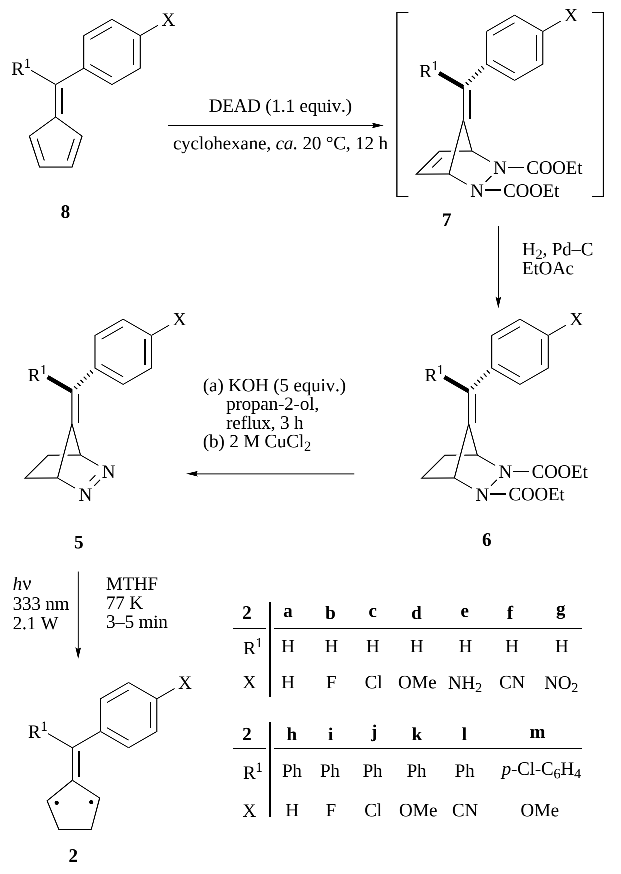
[†] Such cross-conjugated species were first prepared by Schlenk and Brauns.[3]

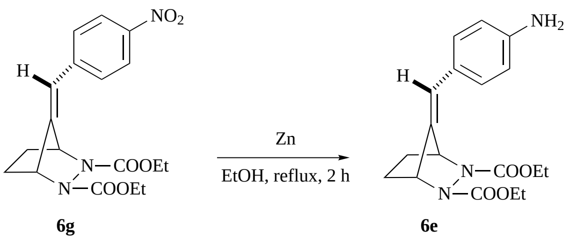
[‡] We also examined some unsymmetrical diaryl-substituted derivatives of **2** ($R^1 = H$, $R^2 = Ar$), which would feature Berson-type TMMs with different aryl group on one and the same radical site to assess captodative effects[10] through the highly sensitive *D* parameter.



2	a	b	c	d	e	f	g
R^1	H	H	H	H	H	H	H
X	H	F	Cl	OMe	NH_2	CN	NO_2

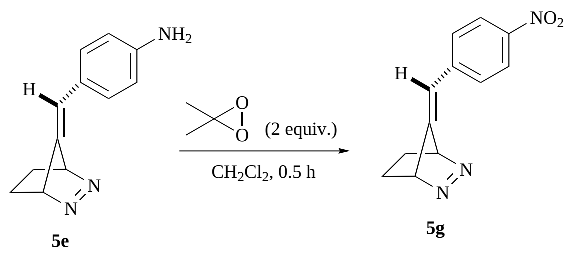
2	h	i	j	k	l	m
R^1	Ph	Ph	Ph	Ph	Ph	*p*-Cl-C_6H_4
X	H	F	Cl	OMe	CN	OMe

the hydrazides **6**. Their saponification and subsequent oxidation afforded the relatively labile diazenes **5**. In the case of **5e** (R^1 = H, X = NH_2), the hydrazide **6e** was prepared by the reduction of the nitro group of hydrazide **6g** [eqn. (2)]. The nitro-



(2)

substituted diazene **5g** (R^1 = H, X = NO_2) was synthesized by the oxidation of **5e** (R^1 = H, X = NH_2) with dimethyldioxirane [eqn. (3)].



(3)

The triplet diradicals **2** were generated from the diazenes **5** by irradiation with 333 nm laser line (2.1 W) in a 77 K 2-methyltetrahydrofuran (MTHF) matrix. The zero-field-splitting (zfs) parameters *D* and *E* were determined from the *X* and *Y* signals of the EPR spectra[13] because the *Z* signals were detected only as shoulders of the *Y* signals (Table 1); the results were checked by simulation. In the case of derivative **2f** (X = CN), the *D* value had to be estimated by simulation (error ±0.0002 cm^{-1}), since the *Z* and *Y* signals were indistinguishable.

Table 1 EPR *D* parameters for the triplet TMM derivatives 2**a**–**g** and the corresponding localized cyclopentane-1,3-diyls **4a**–**g**

X		|*D*/*hc*|/cm^{-1}	
		2[a]	**4**[b]
NO_2	(**2g**)	0.0162	0.0454
CN	(**2f**)	0.0182	0.0477
NH_2	(**2e**)	0.0184	0.0493
OMe	(**2d**)	0.0195	0.0509
Cl	(**2c**)	0.0196	0.0502
H	(**2a**)	0.0196[c]	0.0506
F	(**2b**)	0.0201	0.0514

[a] Measured in MTHF matrix at 77 K, the *D* values were determined from the experimental EPR spectra, error ±0.0001 cm^{-1}, except for **2b** (X = CN), whose *D* value was estimated by simulation, error ±0.0002 cm^{-1}. [b] Taken from ref. 8(*b*). [c] Taken from ref. 4(*a*).

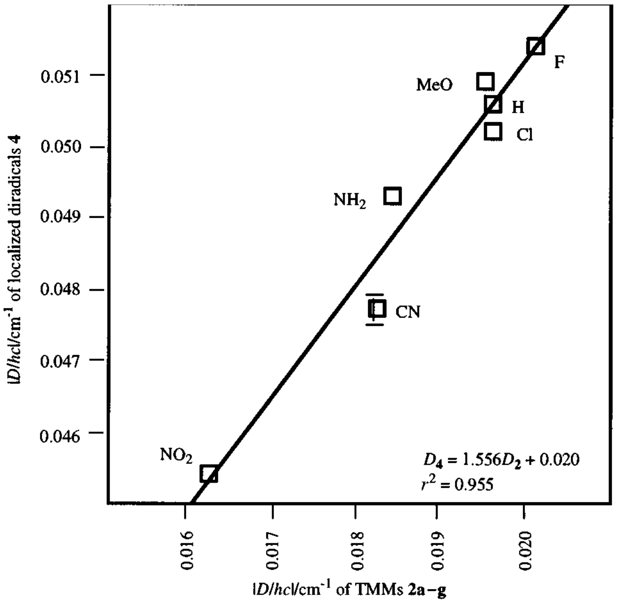


Fig. 1 |*D*/*hc*|/cm^{-1} values of the localized diradicals **4a**–**g** *versus* those of the TMMs **2a**–**g**

As can be seen in Table 1, although the substituents effects on the *D* values are relatively small for the TMM derivatives **2** compared with those of the localized analogs **4**,[8b] a good linear correspondence (r = 0.955, slope m = 1.556) is obeyed (Fig. 1). Thus, as for the localized diradicals **4**, also for this set of substituents, *p*-NO_2 is the best spin acceptor and *p*-F is the worst; in fact, the *D* value of *p*-F is slightly higher than that for the parent (*p*-H), and acts as a spin donor. Interestingly, the *p*-NH_2 group also behaves as spin acceptor for the TMM triplet diradicals **2**, analogously to the localized derivatives **4**.[8b]

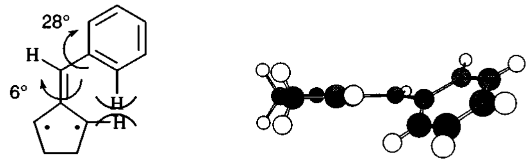
For the set of diaryl-substituted triplets **2h**–**m** (Scheme 1), all the measured *D* values ranged between 0.0176 and 0.0178 cm^{-1}, *i.e.* within experimental error, and the values are indistinguishable from the parent system **2h** (0.0178 cm^{-1}). In view of these negligible electronic substituent effects, all further work on these systems was abandoned.

As is evident in Table 1, the electronic substituent effects on the *D* parameter of the delocalized (cross-conjugated) TMMs **2a**–**g** are relatively small compared with those of the localized triplet diradicals **4**. In simplistic terms, in the localized diradicals **4**, one of the two unpaired spins resides at each of the two radical sites, while in the TMMs **2**, two spins are delocalized over three radical sites. Effectively, two-thirds of the spin density is available in TMMs **2** for electronic perturbation by the substituents. In fact, the slope of 1.556 in Fig. 1 bears out this reduced efficacy of electronic substituent effects for the localized *versus* delocalized diradicals. Additionally, in the TMM structures steric factors must also be considered. While

Table 2 AM1/AUHF-calculated spin densities at the benzylic radical site of the TMMs **2a–g** for both the twisted (ρ_{tw}) and planar (ρ_{pl}) conformation

X		ρ_{tw}	$\Delta\rho_{tw}$[a] $\times 10^2$	ρ_{pl}	$\Delta\rho_{pl}$[b] $\times 10^2$
NO_2	**(2g)**	0.4300	0.47	0.5637	0.82
CN	**(2f)**	0.4328	0.19	0.5683	0.36
NH_2	**(2e)**	0.4340	0.07	0.5664	0.55
OMe	**(2d)**	0.4343	0.04	0.5690	0.29
Cl	**(2c)**	0.4343	0.04	0.5704	0.15
F	**(2b)**	0.4345	0.02	0.5701	0.18
H	**(2a)**	0.4347	0.00	0.5719	0.00

[a] $\Delta\rho_{tw} = \rho_{tw}(H) - \rho_{tw}(X)$. [b] $\Delta\rho_{pl} = \rho_{pl}(H) - \rho_{pl}(X)$.



2a

Fig. 2 AM1-calculated optimized structure of the parent TMM **2a** derivative

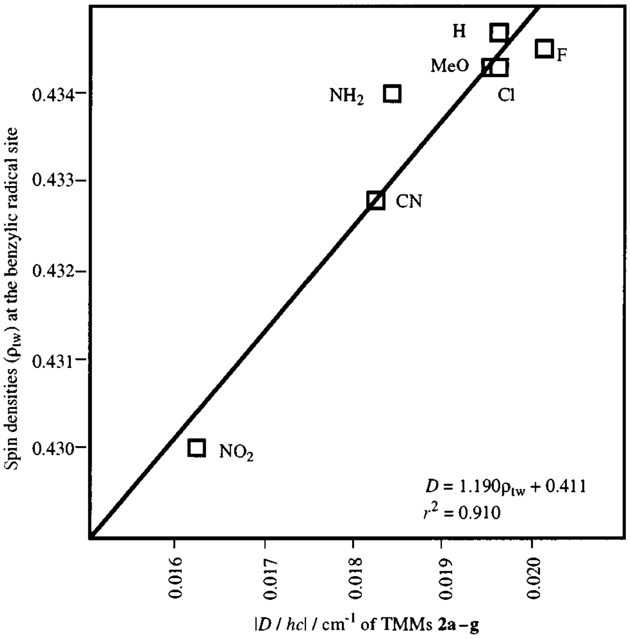


Fig. 3 AM1/AUHF-calculated spin densities (ρ_{tw}) at the benzylic radical site *versus* $|D/hc|/cm^{-1}$ values of the TMMs **2a–g**

the benzylic radical site in the localized triplets **4** is perfectly planar,[8b] severe steric repulsion between the *ortho*-H atoms of the phenyl ring and the hydrogen atoms at the radical sites of the cyclopentane-diyl ring is expected to afford a twisted conformation, and delocalization of the spin into the phenyl ring at the benzylic site should additionally be smaller than in the planar conformation. To confirm this point, the optimized conformation for the **2a** derivative was assessed by the semiempirical AM1[14] method (Fig. 2). As expected, the twisted conformation is lower in energy with the twist angles of *ca.* 28° for the phenyl group and *ca.* 6° around the exomethylene bond. For the other TMMs **2b–g**, the twist angles were to within one degree, the same.

Next, in order to assess quantitatively how much the spin delocalization into the phenyl ring is diminished in the twisted conformation, the spin densities (ρ) at the benzylic radical site were calculated by the AM1/AUHF method for both the twisted (ρ_{tw}) and planar (ρ_{pl}) conformations of the TMMs **2** (Table 2). As expected, the electronic substituent effects on the spin delocalization in the twisted conformation of the TMMs **2**, as expressed by $\Delta\rho_{tw} = \rho_{tw}(H) - \rho_{tw}(X)$, are much smaller (only a half) than those of the planar conformation, as expressed by $\Delta\rho_{pl} = \rho_{pl}(H) - \rho_{pl}(X)$. These results unequivocally establish that the twisted conformation of the phenyl ring in the cross-conjugated TMM triplet diradicals **2** is one of the reasons for relatively small electronic substituent effects on the *D* values, as observed experimentally (Table 1, Fig. 1).

For the localized triplet diradicals **4**, we have shown that the simple expression in eqn. (1) relates the experimental EPR-spectral *D* parameter directly to the theoretical spin densities ρ_A and ρ_B at the benzylic radical sites.[8b] In fact, this convenient relationship allows us to assess the degree of spin delocalization in benzyl-type radicals as a function of the electronic nature of the substituent on the phenyl group.[8b] Of course, it was of interest to check whether such a functional correlation also applies to the cross-conjugated TMMs **2**. Consequently, the computed spin densities (ρ_{tw}) at the benzylic radical sites were plotted against the experimental *D* values for the TMMs **2** (Fig. 3). Indeed, quite good linearity ($r^2 = 0.910$) is observed, with the largest deviations notable for *p*-F and *p*-NH_2. For the former, semiempirical calculations are notoriously less satisfactory for fluorine substituents, while for the *para*-amino group corrections for polar effects probably need to be made.[8e] However, more surprising is the fact that such a good linear correlation is observed at all, because eqn. (1) should be limited to localized triplet diradicals in view of the approximations (neglect of two-center interactions) made in its derivation.[8b] Presumably the spin distribution over the cross-conjugated TMM moiety and spin polarization at the central quaternary carbon atom are relatively insensitive to electronic substituent effects at the benzyl-radical site in these TMM triplet states. It should be instructive to probe this through higher-level computations. At this point we conclude that the electronic substituent effects in the delocalized triplet diradicals **2** parallel those established localized diradicals **4**.

Experimental

General aspects

^1H and ^{13}C NMR spectra were measured on a Bruker AC 200 (^1H, 200 MHz; ^{13}C, 50 MHz) spectrometer with deuteriochloroform as an internal standard. *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. 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 B-545, 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 on a UV-light exposure. Silica gel (63–200 µm; Woelm) was used for column chromatography.

Preparation of the fulvene

The fulvenes **8b–d**[11c] and **8f,g**[12] were synthesized by the reported methods.

Preparation of the cycloadducts 6b–d,f–m

The corresponding fulvene (10 mmol) was dissolved in cyclohexane (50 cm^3) and 1.1 equiv. of diethyl azodicarboxylate (11 mmol) was slowly added at *ca.* 20 °C. The mixture was stirred for 12 h, after which the precipitate was collected by filtration. The white powder, the [4 + 2] cycloadduct **7**, was dissolved in ethyl acetate (100 cm^3), and 10 mg of palladium-on-charcoal catalyst were added. The mixture was stirred under a hydrogen-gas atmosphere (for **7b–d,f,g** 0.5 h, for **7h–m** 1.5 h), the catalyst was removed by the filtration over Celite, and the ethyl acetate was removed at reduced pressure (40 °C at 240 Torr). The solid, except for **6b**, was recrystallized from MeOH (50 cm^3) at −5 °C to give the pure hydrazides **6**, of which derivatives **6d**[15] and **6h**[4a] are known compounds. The hydrazide **6b** was purified by silica-gel chromatography with EtOAc–*n*-hexane (25%) as the eluent.

Diethyl 7-(4-fluorophenylmethylene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (6b). Viscous oil (2.60 g, 75%) (Found: C, 61.95; H, 6.09; N, 8.24. $C_{18}H_{21}FN_2O_4$ requires C, 62.06; H, 6.08; N, 8.04%); ν_{max}(liquid film)/cm^{-1} 2981, 2874, 1747, 1694, 836; δ_H(200 MHz; CDCl$_3$) 1.15–1.47 (6 H, m, *CH*$_3$CH$_2$), 1.75–2.25 (4 H, m, 5- and 6-H), 4.05–4.45 (4 H, m, CH$_3$*CH*$_2$), 4.52–4.80 (1 H, br, 1-H), 4.95–5.35 (1 H, br, 4-H), 6.34 (1 H, s, vinyl), 6.99–7.09 (2 H, br, ArH), 7.26–7.29 (2 H, br, ArH); δ_C(50 MHz; CDCl$_3$) 14.5 (2 × br q, OCH$_2$*C*H$_3$), 26.8 (2 × br t, 5- and 6-CH$_2$), 57.8 (2 × br d, 1- and 4-CH), 62.5 (2 × br t, O*C*H$_2$CH$_3$), 115.5 (2 × dd, J_{CF} 21.5, Ar), 116.3 (d, *C*H=C), 129.8 (2 × d, Ar), 131.7 (s, CH=*C*), 139.3 (s, Ar), 155.2 (2 × s, C=O), 162.1 (d, J_{CF} 246).

Diethyl 7-(4-chlorophenylmethylene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (6c). Colorless powder (3.03 g, 83%), mp 85–86 °C (Found: C, 59.16; H, 5.68; N, 7.63. $C_{18}H_{21}ClN_2O_4$ requires C, 59.26; H, 5.80; N, 7.68%); ν_{max}(KBr)/cm^{-1} 2988, 2939, 1742, 1685, 1492, 1101; δ_H(200 MHz; CDCl$_3$) 1.16–1.45 (6 H, m, *CH*$_3$CH$_2$), 1.62–2.25 (4 H, m, 5- and 6-H), 4.04–4.20 (4 H, m, CH$_3$*CH*$_2$), 4.55–4.85 (1 H, br, 1-H), 4.95–5.38 (1 H, br, 4-H), 6.233 (1 H, s, vinyl), 7.22–7.38 (4 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.4 (2 × br q, OCH$_2$*C*H$_3$), 26.8 (2 ×br t, 5- and 6-CH$_2$), 57.7 (2× br d, 1- and 4-CH), 62.6 (2 × br t, O*C*H$_2$CH$_3$), 116.2 (d, *C*H=C), 128.6 (2 × d, Ar), 129.2 (2 × d, Ar), 133.4 (s, Ar), 134.0 (S, CH=*C*), 140.0 (s, Ar), 154.5 (2 × s, C=O).

Diethyl 7-(4-cyanophenylmethylene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (6f). Colorless powder (2.95 g, 83%), mp 126–127 °C (Found: C, 64.24; H, 5.87; N, 11.96. $C_{19}H_{21}N_3O_4$ requires C, 64.21; H, 5.96; N, 11.82%); ν_{max}(KBr)/cm^{-1} 2981, 2226, 1736, 1705, 1245, 1311, 892; δ_H(200 MHz; CDCl$_3$) 1.23–1.30 (6 H, m, *CH*$_3$CH$_2$), 1.68–2.31 (4 H, m, 5- and 6-H), 4.05–4.38 (4 H, m, CH$_3$*CH*$_2$), 4.61–4.81 (1 H, br, 1-H), 4.95–5.32 (1 H, br, 4-H), 6.40 (1 H, s, vinyl), 7.27–7.50 (2 H, br, ArH), 7.61–7.66 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.3 (2 × br q, OCH$_2$*C*H$_3$), 26.7 (2 × br t, 5- and 6-CH$_2$), 57.7 (2 × br d, 1- and 4-CH), 62.0 (2 × br t, O*C*H$_2$CH$_3$), 111.1 (s, CN), 115.9 (d, *C*H=C), 118.5 (s, Ar), 128.6 (2 × d, Ar), 132.3 (2 × d, Ar), 140.2 (s, CH=*C*), 142.8 (s, Ar), 156.5 (2 × s, C=O).

Diethyl 7-(4-nitrophenylmethylene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (6g). Colorless powder (1.32 g, 35%), mp 89–90 °C (Found: C, 57.31; H, 5.77; N, 11.21. $C_{18}H_{21}N_3O_6$ requires C, 57.59; H, 5.64; N, 11.19%); ν_{max}(KBr)/cm^{-1} 2978, 1742, 1702, 1594, 1512, 891; δ_H(200 MHz; CDCl$_3$) 1.17–1.45 (6 H, m, *CH*$_3$CH$_2$), 1.65–2.25 (4 H, m, 5- and 6-H), 4.01–4.45 (4 H, m, CH$_3$*CH*$_2$), 4.52–4.90 (1 H, br, 1-H), 4.95–5.35 (1 H, br, 4-H), 6.44 (1 H, s, vinyl), 7.28–7.58 (2 H, br, ArH), 8.16–8.21 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.4 (2 × br q, OCH$_2$*C*H$_3$), 26.4 (2 × br t, 5- and 6-CH$_2$), 57.6 (2 × br d, 1- and 4-CH), 62.7 (2 × br t, O*C*H$_2$CH$_3$), 115.5 (d, *C*H=C), 123.9 (2 × d, Ar), 128.8 (2 × d, Ar), 142.2 (s, Ar or CH=*C*), 143.5 (s, CH=*C* or Ar), 146.9 (s, Ar), 156.1 (2 × s, C=O).

Diethyl 7-(4-fluorodiphenylmethylene)-2,3-diazabicyclo-[2.2.1]heptane-2,3-dicarboxylate (6i). Colorless powder (3.78 g, 89%), mp 95–96 °C (Found: C, 67.69; H, 6.20; N, 6.64. $C_{24}H_{25}FN_2O_4$ requires C, 67.91; H, 5.94; N, 6.60%); ν_{max}(KBr)/cm^{-1} 2990, 2908, 1748, 1705, 1603; δ_H(200 MHz; CDCl$_3$) 1.02–1.41 (6 H, m, *CH*$_3$CH$_2$), 1.70–2.22 (4 H, m, 5- and 6-H), 4.05–4.38 (4 H, m, CH$_3$*CH*$_2$), 4.71 (1 H, br s, 1-H), 4.84 (1 H, br s, 4-H), 6.91–7.12 (7 H, m, ArH), 7.22–7.30 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.3 (2 × br q, OCH$_2$*C*H$_3$), 26.7 (2 × br t, 5- and 6-CH$_2$), 60.3 (2 × br d, 1- and 4-CH), 62.3 (2 × br t, O*C*H$_2$CH$_3$), 115.1 (2 × dd, J_{CF} 21.3, Ar), 127.8 (2 × d, Ar), 128.2 (2 × d, Ar), 129.2 (2 × d, Ar), 130.1 (s, *C*=C or Ar), 131.0 (d, Ar), 136.1 (s, Ar or *C*=C), 137.3 (C=*C*), 139.9 (s, Ar), 156.8 (2 × s, C=O), 162.2 (d, J_{CF} 246, Ar).

Diethyl 7-(4-chlorodiphenylmethylene)-2,3-diazabicyclo-[2.2.1]heptane-2,3-dicarboxylate (6j). Colorless powder (3.00 mg, 68%), mp 95–96 °C (Found: C, 65.38; H, 5.71; N, 6.35. $C_{24}H_{25}ClN_2O_4$ requires C, 65.23; H, 5.80; N, 6.26%); ν_{max}(KBr)/cm^{-1} 2980, 1746, 1705, 1317; δ_H(200 MHz; CDCl$_3$) 1.15–1.45 (6 H, m, *CH*$_3$CH$_2$), 1.80–2.23 (4 H, m, 5- and 6-H), 4.05–4.35 (4 H, m, CH$_3$*CH*$_2$), 4.71–4.95 (2 H, br, 1- and 4-H), 7.07–7.12 (4 H, m, ArH), 7.26–7.32 (5 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.4 (2 × br q, OCH$_2$*C*H$_3$), 25.9 (2 × br t, 5- and 6-CH$_2$), 60.2 (2 × br d, 1- and 4-CH), 62.3 (2 × br t, O*C*H$_2$CH$_3$), 127.9 (2 × d, Ar), 128.3 (2 × d, Ar), 128.4 (2 × d, Ar), 129.3 (2 × d, Ar), 130.1 (s, *C*=C or Ar), 130.7 (d, Ar), 133.7 (s, Ar), 137.8 (s, Ar or *C*=C), 138.5 (s, C=*C*), 139.6 (s, Ar), 157.1 (2 × s, C=O).

Diethyl 7-(4-methoxydiphenylmethylene)2,3-diazabicyclo-[2.2.1]heptane-2,3-dicarboxylate (6k). Colorless powder (2.27 g, 52%), mp 52–53 °C (Found: C, 68.51; H, 6.58; N, 6.52. $C_{25}H_{28}N_2O_5$ requires C, 68.79; H, 6.47; N, 6.42%); ν_{max}(KBr)/cm^{-1} 2980, 2908, 1749, 1702, 1607, 1510, 1248, 1058, 827; δ_H(200 MHz; CDCl$_3$) 1.16–1.26 (6 H, m, *CH*$_3$CH$_2$), 1.96–2.10 (4 H, m, 5- and 6-H), 3.75 (3 H, s, OCH$_3$), 4.06–4.15 (4 H, m, CH$_3$*CH*$_2$), 4.80 (2 H, br s, 1- and 4-H), 6.77–6.85 (2 H, m, ArH), 7.02–7.13 (4 H, m, ArH), 7.24–7.27 (3 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.2 (2 × br q, OCH$_2$*C*H$_3$), 28.2 (2 × br t, 5- and 6-CH$_2$), 54.9 (q, O*C*H$_3$), 60.3 (2 × br d, 1- and 4-CH), 62.0 (2 × br t, O*C*H$_2$CH$_3$), 113.3 (2 × d, Ar), 127.5 (2 × d, Ar), 127.9 (2 × d, Ar), 129.1 (2 × d, Ar), 130.4 (s, *C*=C or Ar), 130.6 (d, Ar), 132.2 (s, Ar or *C*=C), 136.1 (s, C=*C*), 140.2 (s, Ar), 156.4 (2 × s, C=O), 158.9 (s, Ar).

Diethyl 7-(4-cyanodiphenylmethylene)-2,3-diazabicyclo-[2.2.1]heptane-2,3-dicarboxylate (6l). Colorless powder (2.33 g, 54%), mp 168–169 °C (Found: C, 69.35; H, 5.77; N, 9.62. $C_{25}H_{25}N_3O_4$ requires, C, 69.59; H, 5.84; N, 9.74%); ν_{max}(KBr)/cm^{-1} 2980, 2226, 1692, 1319, 1008; δ_H(200 MHz; CDCl$_3$) 1.20–1.45 (6 H, m, *CH*$_3$CH$_2$), 1.80–2.22 (4 H, m, 5- and 6-H), 4.10–4.45 (4 H, m, CH$_3$*CH*$_2$), 4.86 (2 H, br s, 1- and 4-H), 7.07–7.12 (2 H, m, ArH), 7.27–7.37 (5 H, m, ArH), 7.37–7.66 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.5 (2 × br q, OCH$_2$*C*H$_3$), 27.5 (2 × br t, 5- and 6-CH$_2$), 60.5 (2 × br d, 1- and 4-CH), 62.5 (2 × br t, O*C*H$_2$CH$_3$), 111.5 (s, Ar), 118.4 (s, CN), 128.3 (2 × d, Ar), 128.5 (2 × d, Ar), 129.3 (2 × d, Ar), 129.6 (s, *C*=C or Ar), 130.1 (d, Ar), 132.1 (2 × d, Ar), 139.1 (s, C=*C*), 139.4 (s, Ar), 144.8 (s, Ar), 155.8 (2 × s, C=O).

Diethyl 7-(4-chloro-4′-methoxydiphenylmethylene)-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (6m). Colorless powder (2.40 g, 51%), mp 59–60 °C (Found: C, 63.89; H, 5.91; N, 5.81. $C_{25}H_{27}ClN_2O_5$ requires C, 63.76; H, 5.78; N, 5.95%); ν_{max}(KBr)/cm^{-1} 2980, 2873, 1749, 1702, 1607, 1511, 1248, 836, 817; δ_H(200 MHz; CDCl$_3$) 1.15–1.38 (6 H, m, *CH*$_3$CH$_2$), 1.85–2.21 (4 H, m, 5- and 6-H), 3.61 (3 H, s, OCH$_3$), 4.18–4.25 (4 H, m, CH$_3$*CH*$_2$), 4.85 (2 H, br s, 1- and 4-H), 6.81–6.89 (2 H, m, ArH), 7.02–7.10 (4 H, m, ArH), 7.28–7.33 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.8 (2 × br q, OCH$_2$*C*H$_3$), 26.5 (2 × br t, 5- and 6-CH$_2$), 55.7 (q, OCH$_3$), 60.9 (2 × br d, 1- and 4-CH), 62.8 (2 × br t, O*C*H$_2$CH$_3$), 114.1 (2 × d, Ar), 129.0 (2 × d, Ar), 130.1 (s, *C*=C), 130.8 (s, Ar), 131.2 (2 × d, Ar), 132.6 (2 × d, Ar), 134.1 (s, Ar), 137.3 (s, Ar), 139.4 (s, C=*C*), 158.4 (2 × s, C=O), 159.8 (s, Ar).

Preparation of cycloadduct 6e

To a solution of cycloadduct **6g** (1.00 g, 2.9 mmol) in 78% EtOH (50 cm^3) was added zinc dust (9.50 g, 50 equiv.) and calcium chloride (0.230 g, 0.7 equiv.) at *ca.* 20 °C. The mixture was allowed to reflux for 2 h, the excess zinc metal was removed by filtration, and the solvent removed under reduced pressure (30 °C, 100 Torr). The desired cycloadduct **6e** was purified by silica-gel chromatography with EtOAc–*n*-hexane (30%) as the eluent.

Diethyl 7-(4-aminophenylmethylene)-2,3-diazabicyclo[2.2.1]-heptane-2,3-dicarboxylate (6e). Yellow powder (810 mg, 74%), mp 64–65 °C (Found: C, 62.31; H, 6.88; N, 12.21. $C_{18}H_{23}N_3O_4$ requires C, 62.59; H, 6.71; N, 12.17%); ν_{max}(KBr)/cm^{-1} 3462, 3368, 2981, 1739, 1518; δ_H(200 MHz; CDCl$_3$) 1.20–1.30 (6 H, m, *CH*$_3$CH$_2$), 1.60–2.02 (4 H, m, 5- and 6-H), 3.64 (2 H, br s, NH$_2$), 4.04–4.30 (4 H, m, CH$_3$*CH*$_2$), 4.45–4.75 (1 H, br, 1-H), 5.25–5.32 (1 H, br, 4-H), 6.22 (1 H, s, vinyl), 6.58–6.64 (2 H, br, ArH), 6.98–7.25 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 14.3 (2 × br q, OCH$_2$*C*H$_3$), 28.0 (2 × br t, 5- and 6-CH$_2$), 57.9 (2 × br d, 1-, and 4-CH), 62.2 (2 × br t, O*C*H$_2$CH$_3$), 114.8 (2 × d, Ar), 117.3 (d, *C*H=C), 125.7 (s, Ar), 129.2 (2 × d, Ar), 135.8 (s, CH=*C*), 146.2 (S, Ar), 156.5 (2 × s, C=O).

Preparation of the diazenes 5b–f,h–m[4a]

Under reflux, to a solution of KOH (25 mmol, 5 equiv.) in degassed propan-2-ol (15 cm^3) was added dropwise a solution of cycloadduct **6** (5 mmol) in degassed propan-2-ol (5 cm^3) under a nitrogen-gas atmosphere. The mixture was stirred for 3 h, cooled to 0 °C, diluted by addition of 100 g of ice–water, and acidified with 5 cm^3 of conc. hydrochloric acid (pH *ca.* 1–2). The pH was adjusted to *ca.* 5–6 by addition of 12% aqueous NH$_3$ solution, 10 cm^3 of 1 M aqueous CuCl$_2$ solution were added and the resulting suspension was recovered by filtration. The dark powder was dissolved in a mixture of 12% aqueous NH$_3$ solution (50 cm^3) and CH$_2$Cl$_2$ (50 cm^3), and the mixture was stirred for 30 min at 0 °C. The organic layer was separated and dried over MgSO$_4$ at 0 °C. The diazene **5** was purified by silica-gel chromatography with EtOAc–*n*-hexane (15%) as the eluent. The spectral data for diazenes **5** are given below, except for derivatives **5d**[15] and **5h**,[4a] which are known.

7-(4-Fluorophenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5b). Colorless plates (525 mg, 52%), mp 68–69 °C with decomposition (Found: C, 71.05; H, 5.40; N, 13.59. $C_{12}H_{11}FN_2$ requires C, 71.27; H, 5.48; N, 13.85%); ν_{max}(KBr)/cm^{-1} 2950, 1601, 1509, 1226, 1162, 1098, 830; λ_{max}(benzene)/nm 342 (ε/M^{-1} cm^{-1} 202), 331 (200); δ_H(200 MHz; CDCl$_3$) 1.19–1.27 (2 H, m, 5- and 6-H), 1.77–1.84 (2 H, m, 5- and 6-H), 5.26 (1 H, br s, 4-H), 5.69 (1 H, br s, 1-H), 6.13 (1 H, s, vinyl), 6.99–7.07 (2 H, m, ArH), 7.13–7.21 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 20.8 (t, 5- or 6-CH$_2$), 21.7 (t, 6- or 5-CH$_2$), 72.6 (d, 1- or 4-CH), 78.1 (d, 4- or 1-CH), 115.6 (2 × dd, J_{CF} 22.4, Ar), 116.5 (d, *C*H=C), 129.6 (2 × d, Ar), 129.8 (s, Ar), 131.7 (s, CH=*C*), 161.5 (d, J_{CF} 295, Ar).

7-(4-Chlorophenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5c). Colorless powder (350 mg, 32%), mp 79–81 °C with decomposition (Found: C, 65.95; H, 5.18; N, 12.65. $C_{12}H_{11}ClN_2$ requires C, 65.91; H, 5.07; N, 12.81%); ν_{max}(KBr)/cm^{-1} 2949, 1492, 1279, 1095, 821; λ_{max}(benzene)/nm 340 (ε/M^{-1} cm^{-1} 144), 331 (123); δ_H(200 MHz; CDCl$_3$) 1.20–1.24 (2 H, m, 5- and 6-H), 1.78–1.83 (2 H, m, 5- and 6-H), 5.24 (1 H, br s, 4-H), 5.67 (1 H, br s, 1-H), 6.11 (1 H, s, vinyl), 7.05–7.15 (2 H, m, ArH), 7.21–7.29 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 20.7 (t, 5- or 6-CH$_2$), 21.7 (t, 6- or 5-CH$_2$), 72.6 (d, 1- or 4-CH), 78.0 (d, 4- or 1-CH), 116.4 (d, *C*H=C), 128.7 (2 × d, Ar), 129.3 (2 × d, Ar), 133.3 (s, CH=*C*), 133.9 (s, Ar), 147.3 (s, Ar).

7-(4-Aminophenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5e). Yellow powder (508 mg, 51%), mp 77–78 °C with decomposition (Found: C, 72.05; H, 6.81; N, 21.19. $C_{12}H_{13}N_3$ requires C, 72.34; H, 6.58; N, 21.09%); ν_{max}(KBr)/cm^{-1} 3457, 3364, 2974, 2944, 1619, 1517, 1297, 1180, 1110, 831; λ_{max}(benzene)/nm 359 (ε/M^{-1} cm^{-1} 151); δ_H(200 MHz; CDCl$_3$) 0.88–1.23 (2 H, m, 5- and 6-H), 1.35–1.50 (2 H, m, 5- and 6-H), 3.14 (2 H, br s, NH$_2$), 4.90 (1 H, d, *J* 2.2, 4-H), 5.52 (1 H, d, *J* 2.2, 1-H), 5.73 (1 H, s, vinyl), 6.24–6.32 (2 H, m, ArH), 6.77–6.83 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 19.9 (t, 5- or 6-CH$_2$), 20.9 (t, 6- or 5-CH$_2$), 71.8 (d, 1- or 4-CH), 77.5 (d, 4- or 1-CH), 113.9 (2 × d, Ar), 116.6 (d, *C*H=C), 127.4 (s, Ar), 128.5 (2 × d, Ar), 142.1 (s, CH=*C*), 145.4 (s, Ar).

7-(4-Cyanophenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5f). Yellow powder (272 mg, 26%), mp 78–79 °C with decomposition (Found: C, 74.38; H, 5.31; N, 20.29. $C_{13}H_{11}N_3$ requires C, 74.62; H, 5.30; N, 20.08%); ν_{max}(KBr)/cm^{-1} 2935, 2225, 1603, 1505, 1416, 884, 830; λ_{max}(benzene)/nm 322 (ε/M^{-1} cm^{-1} 114), 300 (201); δ_H(200 MHz; CDCl$_3$) 1.16–1.27 (2 H, m, 5- and 6-H), 1.77–1.86 (2 H, m, 5- and 6-H), 5.25 (1 H, br s, 4-H), 5.65 (1 H, br s, 1-H), 6.17 (1 H, s, vinyl), 7.25–7.29 (2 H, m, ArH), 7.58–7.62 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 20.7 (t, 5- or 6-CH$_2$), 21.4 (t, 6- or 5-CH$_2$), 72.4 (d, 1- or 4-CH), 77.9 (d, 1- or 4-CH), 110.9 (s, Ar), 116.1 (d, *C*H=C), 118.5 (s, CN), 129.1 (2 × d, Ar), 132.2 (2 × d, Ar), 139.9 (s, CH=*C*), 150.2 (s, Ar).

7-(4-Fluorodiphenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5i). Yellow powder (904 mg, 65%), mp 106–107 °C with decomposition (Found: C, 77.59; H, 5.69; N, 10.09. $C_{18}H_{15}FN_2$ requires C, 77.68; H, 5.43; N, 10.06%); ν_{max}(KBr)/cm^{-1} 2989, 1601, 1507, 1221, 826; λ_{max}(benzene)/nm 341 (ε/M^{-1} cm^{-1} 112), 334 (100); δ_H(200 MHz; CDCl$_3$) 1.16–1.24 (2 H, m, 5- and 6-H), 1.81–1.86 (2 H, m, 5- and 6-H), 5.35 (1 H, br s, 4-H), 5.37 (1 H, br s, 1-H), 6.97–7.05 (7 H, m, ArH), 7.26–7.30 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 21.19 (t, 5- or 6-CH$_2$), 21.23 (t, 6- or 5-CH$_2$), 75.2 (d, 1- or 4-CH), 75.3 (d, 4- or 1-CH), 115.1 (2 × dd, J_{CF} 21, Ar), 127.8 (2 × d, Ar), 128.1 (2 × d, Ar), 129.2 (2 × d, Ar), 130.1 (s, C=C), 130.9 (d, Ar), 135.6 (s, Ar), 139.4 (s, C=C), 143.6 (s, Ar), 162.1 (d, J_{CF} 246, Ar).

7-(4-Chlorodiphenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5j). Colorless powder (988 mg, 67%), mp 98–100 °C with decomposition (Found: C, 73.47; H, 4.84; N, 9.63. $C_{18}H_{15}ClN_2$ requires C, 73.34; H, 5.13; N, 9.50%); ν_{max}(KBr)/cm^{-1} 3030, 1489, 822; λ_{max}(benzene)/nm 343 (ε/M^{-1} cm^{-1} 102), 331 (115); δ_H(200 MHz; CDCl$_3$) 1.20–1.28 (2 H, m, 5- and 6-H), 1.83–1.91 (2 H, m, 5- and 6-H), 5.38 (1 H, br s, 4-H), 5.40 (1 H, br s, 1-H), 6.98–7.07 (4 H, m, ArH), 7.27–7.36 (5 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 21.27 (t, 5- or 6-CH$_2$), 21.34 (t, 6- or 5-CH$_2$), 75.3 (d, 1- or 4-CH), 75.4 (d, 4- or 1-CH), 127.9 (d, Ar), 128.3 (2 × d, Ar), 128.4 (2 × d, Ar), 129.4 (2 × d, Ar), 130.3 (s, C=C), 130.7 (2 × d, Ar), 133.8 (s, Ar), 136.1 (s, Ar), 139.2 (s, C=C), 144.4 (s, Ar).

7-(4-Methoxydiphenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5k). Colorless powder (218 mg, 15%), mp 66–67 °C with decomposition (Found: C, 78.39; H, 6.46; N, 9.87. $C_{19}H_{18}N_2O$ requires C, 78.59; H, 6.25; N, 9.65%); ν_{max}(KBr)/cm^{-1} 2942, 1751, 1607, 1509, 1248, 1033, 826; λ_{max}(benzene)/nm 342 (ε/M^{-1} cm^{-1} 193), 330 (226); δ_H(200 MHz; CDCl$_3$) 1.18–1.26 (2 H, m, 5- and 6-H), 1.82–1.91 (2 H, m, 5- and 6-H), 3.82 (3 H, s, OCH$_3$), 5.38 (1 H, br s, 4-H), 5.45 (1 H, br s, 1-H), 6.83–6.89 (2 H, m, ArH), 6.96–7.09 (3 H, m, ArH), 7.26 (4 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 21.3 (t, 5- or 6-CH$_2$), 21.4 (t, 6- or 5-CH$_2$), 55.3 (q, OCH$_3$), 75.4 (d, 1- or 4-CH), 75.5 (d, 4- or 1-CH), 113.5 (2 × d, Ar), 127.7 (d, Ar), 128.1 (2 × d, Ar), 129.4 (2 × d, Ar), 130.7 (2 × d, Ar), 130.9 (s, C=C), 132.2 (s, Ar), 140.0 (s, C=C), 142.8 (s, Ar), 159.1 (s, Ar).

7-(4-Cyanodiphenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5l). Yellow powder (314 mg, 22%), mp 98–99 °C with decomposition (Found: C, 79.71; H, 5.35; N, 14.91. $C_{19}H_{15}N_3$ requires C, 79.96; H, 5.30; N, 14.73%); ν_{max}(KBr)/cm^{-1} 3028, 2943, 2230, 1605, 1118, 828; λ_{max}(benzene)/nm 343 (ε/M^{-1} cm^{-1} 187), 329 (201); δ_H(200 MHz; CDCl$_3$) 1.24–1.31 (2 H, m, 5- and 6-H), 1.86–1.92 (2 H, m, 5- and 6-H), 5.33 (1 H, br s, 4-H), 5.41 (1 H, br s, 1-H), 6.99–7.04 (2 H, m, ArH), 7.16–7.20 (2 H, m, ArH), 7.26–7.36 (3 H, m, ArH), 7.36–7.65 (2 H, m, ArH); δ_C(50 MHz; CDCl$_3$) 21.2 (t, 5- or 6-CH$_2$), 21.3 (t, 6- or 5-CH$_2$), 75.2 (d, 1- or 4-CH), 75.4 (4- or 1-CH), 111.5 (s, Ar), 118.5 (s, CN), 128.3 (d, Ar), 128.5 (2 × d, Ar), 129.3 (2 × d, Ar), 129.9 (s, C=C), 130.1 (2 × d, Ar), 132.1 (2 × d, Ar), 138.5 (s, C=C), 144.3 (s, Ar), 146.3 (s, Ar).

7-(4-Chloro-4′-methoxydiphenylmethylene)-2,3-diazabicyclo-[2.2.1]hept-2-ene (5m). Colorless powder (439 mg, 27%), mp 81–82 °C with decomposition (Found: C, 70.26; H, 5.08; N, 8.33. $C_{19}H_{17}ClN_2O$ requires C, 70.26; H, 5.28; N, 8.62%); ν_{max}(KBr)/cm^{-1} 3029, 2947, 1508, 1247, 837, 818; λ_{max}(benzene)/nm 341 (ε/M^{-1} cm^{-1} 110), 329 (123); δ_H(200 MHz; CDCl$_3$) 1.02–1.27 (2 H, m, 5- and 6-H), 1.82–1.88 (2 H, m, 5- and 6-H), 3.82 (3 H, s, OCH$_3$), 5.35 (1 H, br s, 4-H), 5.43 (1 H, br s, 1-H), 6.83–6.87 (2 H, m, ArH), 6.93–7.02 (4 H, m, ArH), 7.26–7.33 (2 H, m); δ_C(50 MHz; CDCl$_3$) 21.3 (t, 5- or 6-CH$_2$), 21.4 (t, 6-, 5-CH$_2$), 55.3 (q, OCH$_3$), 75.4 (2 × d, 1- and 4-CH), 113.7 (2 × d, Ar), 128.4 (2 × d, Ar), 129.8 (s, Ar), 130.6 (2 × d, Ar), 130.7 (2 × d, Ar), 131.7 (s, C=C), 133.7 (s, Ar), 138.4 (s, C=C), 143.3 (s, Ar), 159.3 (s, Ar).

Preparation of diazene 5g

To a solution of diazene **5e** (160 mg, 0.8 mmol) in dry CH_2Cl_2 (30 cm^3) was added slowly a solution of dimethyldioxirane[16] (1.6 mmol, 2 equiv.) in acetone (21 cm^3) at *ca.* 20 °C. The mixture was stirred for 30 min, after which the solvent was removed at reduced pressure (30 °C, 100 Torr) and the desired diazene **5g** (156 mg, 85%) was purified by recrystallization from MeOH at −5 °C.

7-(4-Nitrophenylmethylene)-2,3-diazabicyclo[2.2.1]hept-2-ene (5g). Yellow powder, mp 85–86 °C with decomposition (Found: C, 62.56; H, 4.89; N, 18.33. $C_{12}H_{11}N_3O_2$ requires C, 62.87; H, 4.84; N, 18.33%); ν_{max}(KBr)/cm^{-1} 2946, 1599, 1516, 1344, 1108, 883; λ_{max}(benzene)/nm 348 (ε/M^{-1} cm^{-1} 121), 331 (115); δ_H(200 MHz; $CDCl_3$) 1.24–1.33 (2 H, m, 5- and 6-H), 1.75–1.89 (2 H, m, 5- and 6-H), 5.29 (1 H, br s, 4-H), 5.69 (1 H, br s, 1-H), 6.25 (1 H, s, vinyl), 7.30–7.41 (2 H, m, ArH), 8.16–8.22 (2 H, m), δ_C(50 MHz; $CDCl_3$) 20.8 (t, 5- or 6-CH_2), 21.5 (t, 6- or 5-CH_2), 72.5 (d, 1- or 4-CH), 78.1 (d, 4- or 1-CH), 115.8 (d, *C*H=C), 123.9 (2 × d, Ar), 128.6 (2 × d, Ar), 141.9 (s, CH=*C*), 146.9 (s, Ar), 151.1 (s, Ar).

Computations

Full geometry optimization of the TMM derivatives **2** was carried out by use of the AM1 method and AUHF wavefunction,[17] which are provided in the VAMP 5.0 program,[18] and run on an IRIS INDIGO Silicon Graphics Workstation. Excellent spin expectation $\langle S^2 \rangle$ values of 2.00 were obtained for the spin densities of these radicals.

EPR spectroscopy

A sample (1.5×10^{-2} mmol) of the diazene **5** was dissolved in 0.4 cm^3 of degassed MTHF and transferred to a 3 × 25 mm quartz EPR tube which was then sealed and, to prepare the matrix sample, cooled at 77 K by liquid nitrogen. The triplet diradicals **2** were generated by irradiation with the 333 nm line of an INNOVA-100 CW argon-ion laser (2.1 W, 3–5 min) at 77 K. The EPR spectrum was recorded on a Bruker ESP-300 spectrometer (9.34 GHz, spectra accumulation with the Bruker 1620 data system). The *D* values were determined by a manual analysis of the *X*, *Y* signals or the *Z* signals and checked by simulation with Bruker's WIN-EPR SimFonia Version 1.2. The error limits are ±0.0002 cm^{-1}.

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