A Simple Route to *cis*- and *trans*-Bis-σ-homobenzenes

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Dedicated Professor Leopold Horner on the occasion of his 90th birthday

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Photolysis of tetracyclic azo compounds **15**, readily available from [4+2] cycloaddition between 1,2,4,5-tetrazines and cyclopropenes, gives access to *cis*- and *trans*-bis-σ-homobenzenes **16** and **17**. Thermal transformation of the *cis* isomers **16** affords *cis*,*cis*,*cis*-1,3,6-cyclooctatrienes **18**. Kinetic data for these [σ2s+σ2s+π2s] cycloreversions are reported.

Introduction

The concept of homoaromaticity was first introduced by Winstein in 1959[1] and proved to be an extremely stimulating prospect. Initially, the new concept was especially of interest in the field of carbocations,[2,3] but homoaromaticity quite soon also turned out to be a stimulating guide for the synthesis of new and interesting compounds in the field of carbanions and neutral species.[4,5]

The first attractive goal was triquinacene (**1**). As early as 1964, Woodward designed a multistep synthesis for **1**, in which three double bonds, positioned in a rigid skeleton, should provide valuable information about the phenomenon of homoaromaticity.[6] Several additional syntheses followed,[5] but only Deslongchamps et al.[7,8] and Cook et al.[9,10] succeeded in designing synthetic pathways that allowed satisfactory yields of **1** on multigram scales.

Thermodynamic and theoretical studies showed that, according to its spectroscopic and structural data, the hydrocarbon **1** was definitely not homoaromatic.[5] Nevertheless, triquinacene (**1**) showed its usefulness as a precursor for the synthesis of a variety of hydrocarbons with interesting chemical and structural properties.[5] Diademane (**2**) proved not to be obtainable by means of an envisaged threefold internal photochemical cycloaddition of triene **1**, but de Meijere et al.[11,12] developed an independent synthetic route. Thermally labile diademane (**2**) could be isolated using this route, but at 80 °C it quickly transformed into triquinacene (**1**) through a [σ2s+σ2s+σ2s] cycloreversion. Although the unbridged analogue *cis*-tris-σ-homobenzene (**3a**) is still unknown, a wide variety of derivatives such as **3b**−**3d** have been synthesized by Prinzbach and co-workers, demonstrating the stabilizing effect of electron-withdrawing substituents R.[13] At elevated temperatures, **3b**−**3d** undergo clean cycloreversion to all-*cis*-1,4,7-cyclononatrienes, in analogy to the transformation **2** → **1**. In contrast, *trans*-tris-σ-homobenzene (**4**) is stable at high temperatures (350 °C) and only isomerizes by flow pyrolysis at 380−400 °C, presumably by way of *cis*,*trans*,*trans*-1,4,7-cyclononatriene as the first nonisolable compound.[5,14]

In an excellent comprehensive investigation, Prinzbach[15−18] and Vogel[19,20] established routes to heteroanalogues of *cis*- and *trans*-tris-σ-homobenzenes **3a** and **4**. Oxa, aza and thia derivatives such as **5** and **6** (Figure 1) could be isolated, demonstrating the stabilizing effect of electron-withdrawing substituents for the tris-σ-homobenzene framework. The tendency of the tris-σ-homobenzene skeleton to ring-open was again much more pronounced in the *cis* series **5** than in the *trans* isomers **6**.

The high tendency of **2** and **3** to ring-open carries over to the first lower homologue **7**. *cis*-Bis-σ-homobenzene (**7**) is still unknown, while the *trans* isomer **8** was synthesized quite early and proved to be a stable molecule up to 300 °C (above this temperature, isomerization to 1,3,6-cyclooctatriene occurs).[21,22]

Hetero-bis-σ-homobenzenes **9** and **10** profit from the stabilizing effects of the electron-withdrawing bridges X and Y. A great variety of such compounds have been synthesized; the *cis* isomers **9** cleanly undergo [σ2s+σ2s+π2s] cycloreversions, making interesting conjugated eight-membered heterocyclic trienes available.[23−32]

Whitlock and Schatz proposed *cis*-bis-σ-homobenzenes **11** as reaction intermediates as early as 1971. Even at −78 °C and with two electron-withdrawing groups R, compound **11** furnished the isomeric monocyclic dimethyl 1,4,6-cyclooctatriene-1,2-dicarboxylate by ring opening.[33] Kaupp and Rösch were the first to isolate the pure isomeric *cis*-bis-σ-homobenzene derivative **12**, which was reported to be stable in the crystalline state.[34] In solution, an equilibrium of 80% **12** and 20% of the cyclooctatriene isomer was formed. The thermal stability of the stable bis-σ-homobenzenes **13** and **14** prepared by Menke and Hopf is certainly the result of the additional molecular bridges acting as rate-retarding elements.[35]

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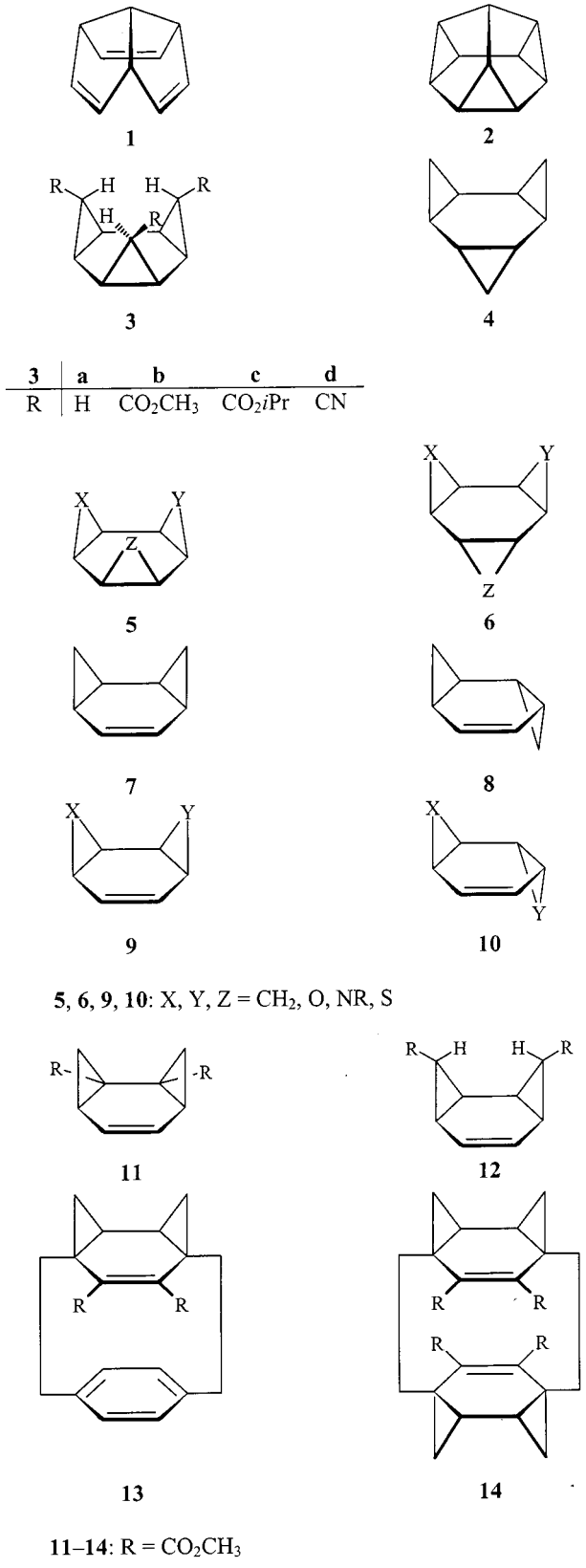


Figure 1. Tris- and bis-σ-homobenzenes

Here we report on a new synthetic route to substituted *cis*-bis-σ-homobenzene derivatives by an unexpected cycloaddition/cycloelimination sequence including a sigmatropic cyclopropane ring shift.[36]

Results and Discussion

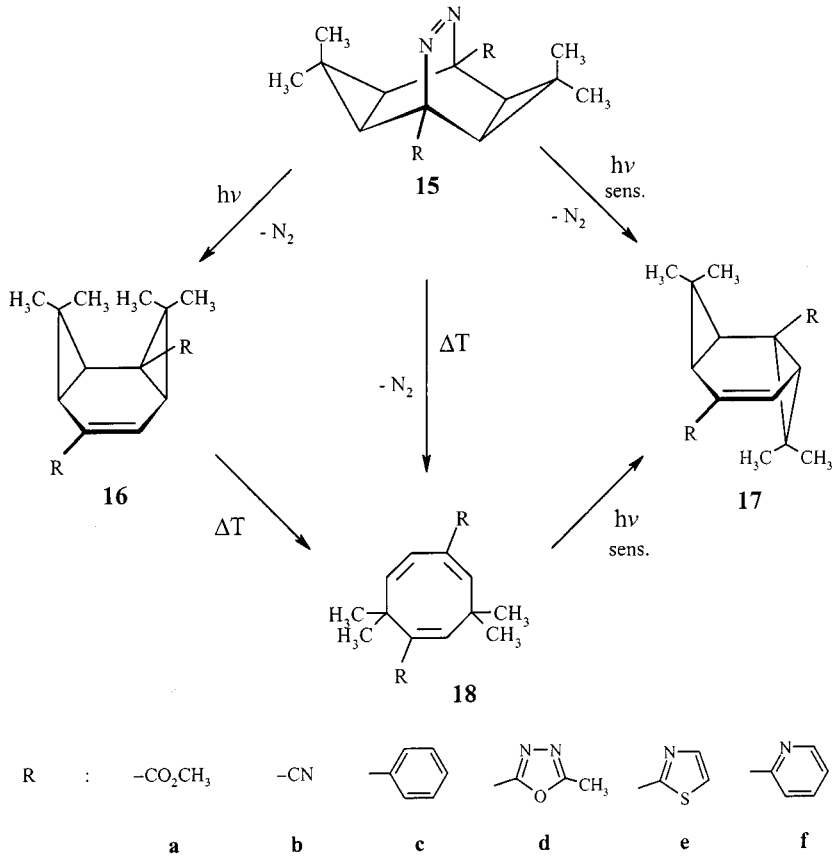
We recently published a general and variable route to tetracyclic azo compounds. The key steps involve a cycloaddition sequence utilising 1,2,4,5-tetrazines and cyclopropenes as starting materials. These produce 3,4-diazanorcaradienes, which react with a second equivalent of cyclopropene as 2π components.[37] In general, a wide variety of azo compounds provided homotropilidenes smoothly on photolysis.[38]

When 3,3-dimethylcyclopropene was used as a dienophile under forcing conditions (high pressure, for example), azo compounds of structure **15** were isolated. Quite unexpectedly, direct photolysis of **15** produced isomers of homotropilidenes. Extensive spectroscopic analysis and further investigation (vide infra) revealed the structures of the isolated compounds as the bis-σ-homobenzene derivatives **16a, 16c, 16d** and **16f** (Scheme 1). Bis-σ-homobenzenes **16b** and **16e** could not be obtained in the crystalline state; the isomeric 1,3,6-cyclooctatrienes **18** were observed instead under the very mild workup conditions. After photolysis of **15b**, the reaction solution showed a strong peak in the HPLC chromatogram; this peak transformed within 5 h at room temperature into a second peak, representative of 62% of **18b**. We assume that the primary photoproduct formed in solution is **16b**.

^{1}H NMR spectra, collected in Table 1 for **16a**, **16c**, **16d** and **16f**, and ^{13}C NMR spectra (see Exp. Sect.) offer convincing structural evidence and need no detailed discussion. Only a signal for one olefinic proton (δ = 6.62−7.96) and three signals for cyclopropane protons (2-H, 4-H, 7-H) are found, with the expected coupling constants, thus ruling out the expected homotropilidene photoproducts.[38] NOEs were of special significance for evidence of the proximity of the corresponding functional groups, with the strong NOE between 10-CH_3 and 11-CH_3 for the bis-σ-homobenzene **16d**, as listed in Figure 2, convincingly attesting to the *cis* configuration.

If the photoreaction of **15** was performed in acetone as solvent, the *trans* isomeric bis-σ-homobenzenes **17** were produced in three systems (**17a**, **17b**, **17d**). In these cases, structural assignment is based not only on ^{1}H and ^{13}C NMR spectra and NOE experiments (Table 2), but also on an X-ray structure analysis obtained for **17b**.[36] NOE experiments, as shown for **17d** in Figure 3, demonstrate the large separation of 10-CH_3 and 11-CH_3 and the proximity of 9-CH_3 and protons 2-H and 4-H, resulting from the *trans* arrangement of the two cyclopropane units in **17d**.

In accordance with their *cis*-bis-σ-homobenzene structures, compounds **16** exhibited the expected thermal lability (Scheme 2). As already mentioned, **16b** and **16e** could not be isolated but were transformed under the mild workup conditions into 1,3,6-cyclooctatriene derivatives. The same isomerization was observed for all other *cis*-bis-σ-homo-

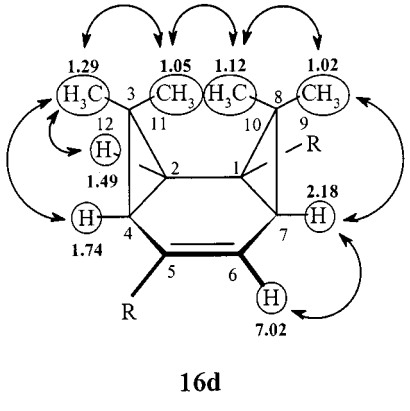


Scheme 1. Conversion of azo compounds by thermally or photochemically induced N_2 elimination

Table 1. ^{1}H NMR chemical shifts [δ values; $CDCl_3$/TMS; 90, 250 or 400 MHz] and coupling constants $J(^1H,^1H)$ [Hz] of *cis*-bis-σ-homobenzenes **16**

No.	δ(3,8-CH_3)	δ(2-H)	δ(4-H)	δ(7-H)	δ(6-H)	^3J(2-H,4-H)	^3J(6-H,7-H)	^4J(4-H,6-H)
16a[a]	1.21, 1.31, 1.39, 1.44 (s)	1.98 (d)	1.90 (dd)	2.26 (d)	7.96 (dd)	8.0	3.7	0.9
16c	0.84, 1.10, 1.11, 1.24 (s)	1.35 (d)	1.43 (dd)	1.63 (d)	6.62 (dd)	8.3	3.9	0.7
16d[b]	1.02, 1.05, 1.12, 1.29 (s)	1.49 (d)	1.74 (ddd)[c]	2.18 (dd)[c]	7.02 (dd)	8.1	3.9	1.1
16f	0.85, 1.08, 1.16, 1.30 (s)	1.44 (d)	1.54 (dd)	1.92 (d)	7.38 (dd)	8.2	3.9	0.9

[a] After addition of $Eu(fod)_3$. – [b] In CD_2Cl_2. – [c] Long-range coupling constant ^5J(7-H/4-H) = 1.0 Hz.



16d

Figure 2. NOEs and chemical shifts (ppm) observed for **16d**

benzenes **16** isolated. For **16a**, **16d** and **16f**, we were also able, using HPLC, to perform kinetic measurements to follow the [σ2s+σ2s+π2s] cycloreversion to 1,3,6-cyclooctatrienes **18** in acetonitrile between 60 and 100 °C. Rate constants k_1 and the activation parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are presented in Table 3. In one case we were also able to demonstrate that the high-temperature pyrolysis of the tetracyclic azo compounds **15** ultimately results in 1,4,6-cyclooctatriene **18**. If **15b** was melted and the melt heated to 250 °C under reduced pressure, **18b** was produced in 30% yield.

Table 4 lists all ^{1}H NMR spectroscopic data for the cyclooctatrienes **18**. Two olefinic protons (2-H and 4-H) appear as singlets with very weak long-range coupling, while 6-H and 7-H show the expected AB system. 1,4,6-Cyclooctatriene, according to Anet and Yavari,[39] exists in a "twist-

Table 2. ^{1}H NMR chemical shifts [δ values; $CDCl_3$/TMS; 90, 250 or 400 MHz] and coupling constants $J(^1H,^1H)$ [Hz] of *trans*-bis-σ-homobenzenes **17**

No.	δ(3,8-CH_3)	δ(2-H)	δ(4-H)	δ(7-H)	δ(6-H)	^3J(2-H,4-H)	^3J(6-H,7-H)	^4J(4-H,6-H)
17a[a]	1.24, 1.38, 1.39, 1.42 (s)	2.13 (d)	1.86 (d)	2.38 (d)	7.74 (d)	8.9	5.5	–
17b	1.20, 1.24, 1.28, 1.44 (s)	1.25 (d)	1.42 (d)	1.61 (d)	6.48 (d)	8.8	5.3	–
17d	0.85, 1.12, 1.24, 1.29 (s)	1.69 (d)	1.78 (d)	2.16 (d)	6.71 (d)	8.7	5.5	–

[a] After addition of $Eu(fod)_3$.

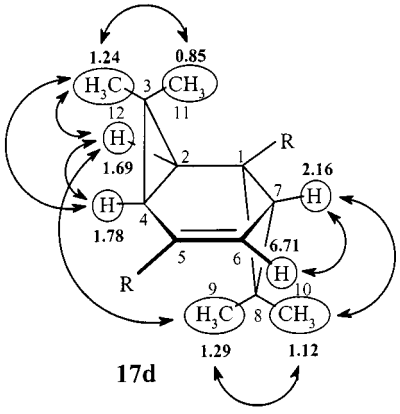
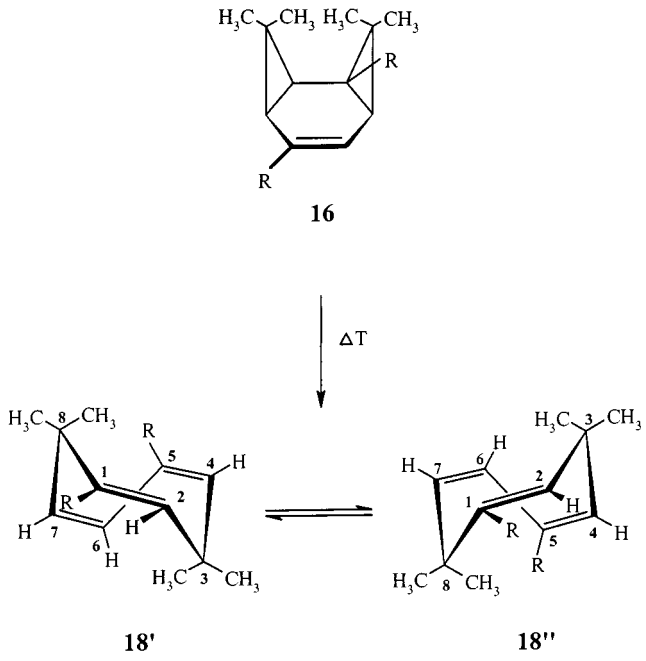


Figure 3. NOEs and chemical shifts (ppm) observed for **17d**

boat-chair'' conformation with a $\Delta G^{\neq}$ value for the rapid ring inversion of 4.1 kcal/mol. The assignment of the signals for the methyl groups at C-3 and C-8 are based on NOESY experiments. While the sharp signal for 3-CH_3 indicates a rapid exchange, the signal for 8-CH_3 shows some broadening at room temperature, indicating that the ring-inversion process for **18** is slower than that of the parent compound. In two cases (**18a**, **18b**) we were able to show by HPLC analysis that these 1,3,6-cyclooctatriene derivatives undergo an intramolecular photochemical [4+2] cycloaddition reaction in acetone solution to form the *trans*-bis-σ-homobenzenes **17a** and **17b**.

How can the experimental results be interpreted? Aliphatic azo compounds are known to be suitable precursors for energy-rich intermediates and compounds of unusual



Scheme 2. Thermally induced [σ2s+σ2s+π2s] cycloreversion **16** → **18**

structure, the initial step being thermal or photochemical nitrogen extrusion.[40–46] The principal mechanistic question for thermal and photochemical decomposition of azoalkanes is one of one-bond versus two-bond cleavage during the denitrogenation via a diazenyl biradical in the former case, finally leading to biradicals.[40] In the last few

Table 3. Rate constants k_1 at different temperatures, k_{298K} and activation parameters $\Delta G^{\neq}_{298}$, $\Delta H^{\neq}$ [kcal·mol^{-1}] and $\Delta S^{\neq}$ [cal·K^{-1}·mol^{-1}] for cycloreversion reaction **16** → **18**

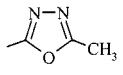
Reaction **16** → **18**	R	$k_1 \cdot 10^5$ [L·mol^{-1}·s^{-1}]	T [K]	$k_{298\,K}$ [s^{-1}]	$\Delta G^{\neq}_{298}$ [kcal·mol^{-1}]	$\Delta H^{\neq}$ [kcal·mol^{-1}]	$\Delta S^{\neq}$ [cal·K^{-1}·mol^{-1}]
16a → **18a**	–COOMe	5.67 ± 0.03 17.2 ± 0.1 77.5 ± 0.1	333.5 343.3 357.1	$4.49 \cdot 10^{-7}$	26.1 ± 0.2	25.6 ± 0.3	–1.6 ± 1.0
16d → **18d**		5.22 ± 0.03 26.2 ± 0.1 222 ± 2.0	328.1 343.1 363.1	$10.4 \cdot 10^{-7}$	25.6 ± 0.2	24.7 ± 0.3	–3.1 ± 1.0
16f → **18f**		5.53 ± 0.24 22.8 ± 0.2 124 ± 2.0	345.9 358.4 374.8	$0.83 \cdot 10^{-7}$	27.1 ± 0.2	27.1 ± 0.3	0.2 ± 1.0

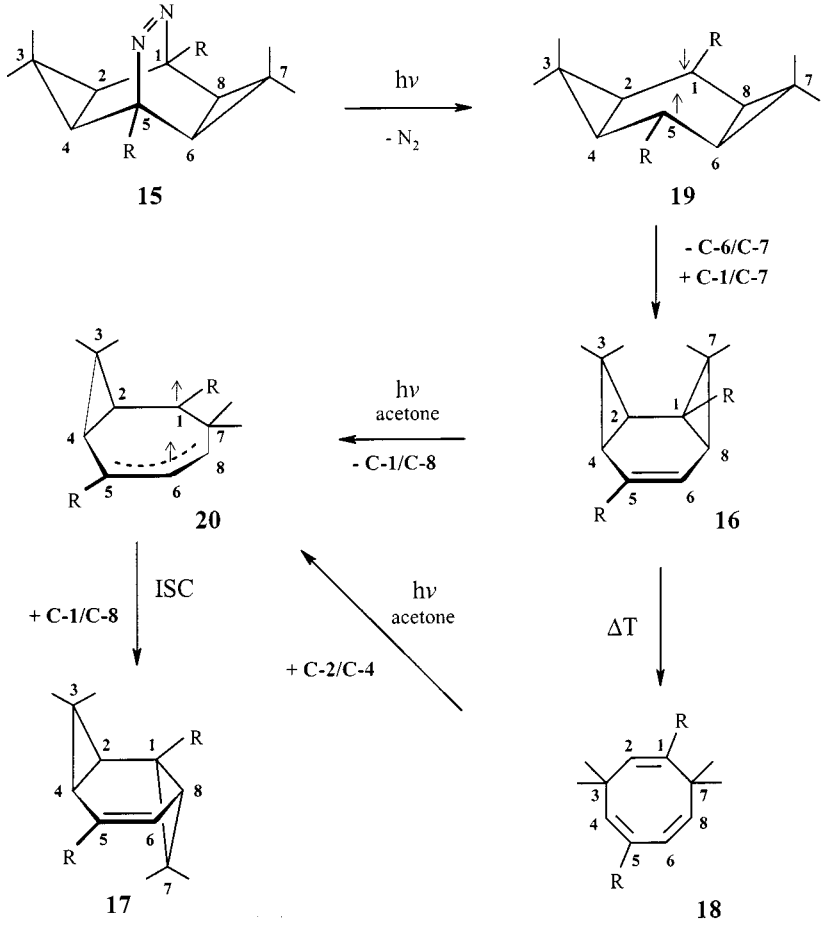
Table 4. ^{1}H NMR chemical shifts [δ values; $CDCl_3$/TMS; 90, 250 or 400 MHz] and coupling constants $J(^1H,^1H)$ [Hz] of 1,3,6-cyclooctatrienes **18** (atom numbering corresponds to Scheme 2)

No.	δ(3-CH_3/8-CH_3)	δ(2-H)	δ(4-H)	δ(7-H)	δ(6-H)	^4J(4-H,2-H)	^3J(7-H,6-H)	^4J(6-H,4-H)
18a	1.30, 1.32 (s)	5.74 (d)	6.62 (dd)	5.58 (d)	6.30 (dd)	0.6	11.3	0.9
18b	1.35, 1.45 (s)	6.31 (d)	6.23 (br. s)	5.68 (d)	6.09 (dd)	0.6	11.2	1.0
18c	1.14, 1.35 (s)	5.34 (br. s)	5.87 (br. s)	5.70 (d)	6.26 (dd)	—[a]	11.3	0.5
18d[b]	1.27, 1.41 (s)	6.01 (d)	6.43 (dd)	5.78 (d)	6.46 (dd)	0.6	11.3	0.9
18e	1.32, 1.41 (s)	6.47 (br. s)	5.79 (br. s)	5.83 (d)	6.49 (d)	—[a]	11.4	—[a]
18f	1.08, 1.42 (s)	6.58 (br. s)	5.43 (br. s)	5.80 (d)	6.45 (d)	—[a]	11.2	—[a]

[a] Not resolved. — [b] In CD_2Cl_2.

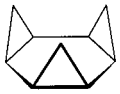
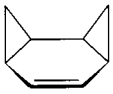
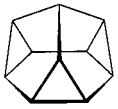
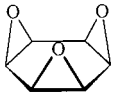
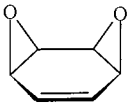
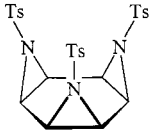
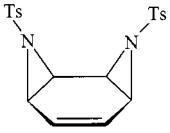
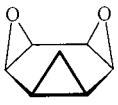
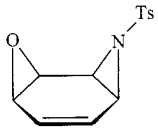
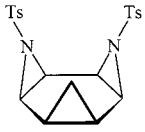
years, however, a consensus of opinion in favour of stepwise elimination of nitrogen has been emerging on both the theoretical and the experimental fronts.

In the photolysis of azoalkanes, many interesting examples of spin-correlation effects on product distribution have been reported,[40,45,47] demonstrating that the singlet and triplet pathways result in products of different structure or different product mixtures. Detailed photomechanistic investigations in the systems studied by us are still awaited. However, it is reasonable to assume that the photoextrusion of nitrogen from **15** on direct photolysis is initiated by the excitation of the weak n → π* absorption of the azochromophore to form an excited singlet state, which rapidly loses nitrogen to form a singlet biradical **19** (Scheme 3).[48] A subsequent, rapid 1,3-carbon shift directly produces the *cis*-bis-σ-homobenzenes **16**, the first isolable products. For a *cis*/*trans* isomerization **16** → **17**, carbon bond C-1−C-8 must be opened. We assume that the triplet biradical **20** is formed in the sensitized photoreaction, and that this, after conformational change, intersystem crossing (ISC) and C-1−C-8 ring closure, opens the way to *trans*-bis-σ-homobenzenes, which can also be obtained by the triplet pathway



Scheme 3. Possible mechanistic pathways for the formation of *cis*- and *trans*-bis-σ-homobenzenes **16** and **17**; the numbering system displayed in this scheme allows us to follow the fate of the carbon atoms in all transformations but is not representative of the IUPAC nomenclature

Table 5. Activation parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$ [kcal·mol^{-1}] and $\Delta S^{\neq}$ [cal·K^{-1}·mol^{-1}] for the [σ2s+σ2s+σ2s] and [σ2s+σ2s+π2s] cycloreversion of *cis*-tris-σ-homobenzenes and *cis*-bis-σ-homobenzenes

Structure	Compd.	$\Delta G^{\neq}$ (T [K]); $\Delta H^{\neq}$; $\Delta S^{\neq}$	Ref.	Structure	Compd.	$\Delta G^{\neq}$ (T [K]); $\Delta H^{\neq}$; $\Delta S^{\neq}$	Ref.
	**3a**	ca. 22 (273);[a] –; –	[13,16]		**7**	ca. 19 (251); –; –	[24]
	**1**	29.1 (333); 31.0; +6.5	[12]		**23**	ca. 22[b]	[13]
	**19**	38.0 (508); –; –	[16]		**25**	25.6 (333); 26.3; +2	[24]
	**20**	31.6 (423); –; –	[16]		**26**	25.0 (333); 22.0; –7.4	[24]
	**21**	32.8 (413); –; –	[16]		**27**	24.9 (333); 27.5; +7.6	[24]
	**22**	28.6 (388); –; –	[16]				

[a] Extrapolated value. – [b] Value for E_A [kcal·mol^{-1}].

starting from cyclooctatrienes **18**. The isolation of *cis*-bis-σ-homobenzenes **16b** and **16e** was precluded even under mild photoreaction and workup conditions, due to their thermal instabilities.

The thermal lability of *cis*-tris- and *cis*-bis-σ-homobenzenes is a phenomenon well-known in the literature. A selection of kinetic data is presented in Table 5. As mentioned earlier, neither *cis*-tris-σ-homobenzene **3a** nor *cis*-bis-σ-homobenzene **7** could be isolated. Electron-withdrawing substituents slightly increase the stability. Much more pronounced is the stabilizing effect of heteroatoms in the three-membered rings, as shown for trioxa and triaza or dioxa and diaza derivatives, such as **19**–**22** or **25**–**27**. The electronegativity of the heteroatoms can be used as a semiquantitative guide for the prediction of the thermostability.

For *cis*-bis-σ-homobenzenes **16a**, **16d** and **16f** we were able to follow the [σ2s+σ2s+π2s] cycloreversion **16** → **18** by kinetic measurements (Table 3). The stabilizing effect of the substituents R increases in the series R = oxadiazolyl < CO_2CH_3 < 2-pyridyl, as demonstrated by the increasing $\Delta G^{\neq}$ values, which slightly surpass the $\Delta G^{\neq}$ values for the hetero-bis-σ-homobenzenes **25**–**27**. Values for the activation entropies $\Delta S^{\neq}$ have been reported in the literature; rather small values of around zero were found (Table 5). As the $\Delta S^{\neq}$ values for the systems **16a**, **16d** and **16f** (Table 3) are in accordance with literature data we conclude, in analogy with literature discussion, that the thermal transformations **16** → **18** occur in a concerted manner.

Conclusion

Tetracyclic azo compounds **15** are photolysed to *cis*-bis-σ-homobenzenes **16** in a singlet reaction. The corresponding *trans* isomers **17** can be obtained in triplet photoreactions starting with azo compounds **15**, *cis*-bis-σ-homobenzenes **16** or 1,3,6-cyclooctatrienes **18**. The activation parameters for the [σ2s+σ2s+π2s] cycloreversions **16**–**18** are in accordance with concerted bond reorganizations.

Experimental Section

General Remarks: IR spectra were recorded with a Beckman Acculab 1 spectrophotometer, and UV/Vis spectra with a Carl Zeiss Specord M500 UV machine. − NMR spectra were obtained with Bruker WH 90, AC 250 and ARX 400 instruments (90 MHz/250 MHz/400 MHz for ^{1}H and 22.63 MHz/63 MHz/100 MHz for ^{13}C); δ values are reported in ppm downfield from the tetramethylsilane signal, and s, d, dd, dt and m indicate singlet, doublet, doublet of doublets, doublet of triplets and multiplet. The degree of substitution of the C atoms was determined by DEPT-135 and DEPT-90 methods and indicated as quat. C, =CH, −CH_2−, −CH_3. − Mass spectra were measured at an ionizing voltage of 70 eV by electron impact with a Varian MAT311A instrument. − Melting points were determined either with a Büchi melting point apparatus (< 280 °C) or with a copper block (> 280 °C) and are uncorrected. − Elemental analyses were performed in the microanalytical laboratory of the University of Regensburg, with Heraeus Mikro U/E and CHN-Rapid instruments. In some cases, for oily compounds in particular, correct elemental analyses could not be obtained, i.e., for **16c**, **17a**, **18b**, **18c** and **18e**. − For analytical thin layer chromatography, precoated plastic sheets (POLYGRAM SIL G/UV 254, Macherey & Nagel) were used. − Silica gel 60 (particle size 0.040−0.063 nm, Merck) was used for flash column chromatography (FC). − Reactions were carried out under nitrogen. Reaction solvents were dried according to standard procedures. The petroleum ether (PE) used had a boiling range of 40−60 °C.

HPLC Kinetic Measurements: Separate solutions of pure (> 99% by HPLC analysis) *cis*-bis-σ-homobenzenes (**16a**, **16d**, **16f**) were prepared in degassed CH_3CN (Baker) at 20.0 °C. One of the solutions of each system (calibration solution) also contained a defined amount (m_{Tr}) of the internal tracer benzophenone (system **16a**) or diphenylacetonitrile (systems **16d/16f**). Solutions, usually containing $0.67-1.94\times10^{-2}$ mol L^{-1} of **16a**, **16d** or **16f**, were divided into 0.5−1.5 mL samples, sealed in small glass tubes and heated to the reaction temperature. Usually, 20 samples were taken at appropriate time intervals and injected into reversed-phase HPLC systems run under various solvent-gradient programs. Reaction progress, usually covering 0−99% of the reaction, was monitored by integration of the relevant signal peaks referring to starting compound and isomerization product, relative to the value obtained for the internal standard. From these integrals (F_i, F_{tr}), the corresponding masses m_i were obtained according to the equation $m_i = m_{tr}\ KF_i\ (F_i/F_{Tr})$, with parameters KF_i provided by independent calibration runs.

General: Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined graphically from values for k_1 at different temperatures, using linear least-squares computer simulation for first-order reactions. Parallel runs were carried out to reproduce the rate constants within less than ± 2%.

General Procedure 1: The photolysis was carried out in a water-cooled immersion-well photoreactor constructed from quartz. The photoreactor was equipped with a medium-pressure mercury lamp (HPK 125 W; Philips) and a Pyrex filter. The photoactive compound was dissolved in an inert solvent (vide infra) and photolysed under magnetic-stirring conditions (reaction times: see below).

General Procedure 2: The photochemical reaction was carried out using an optical bench arrangement, utilizing a focused high-pressure lamp (type HBO-200/500 W; Osram) and a glass filter (λ_{max}: vide infra; Schott). The reactant was dissolved in an inert solvent (vide infra) and irradiated whilst stirring in a water-cooled quartz cell (reaction times: see below).

Dimethyl *cis*-Tricyclo[5.1.0.0^{2,4}]oct-5-ene-1,5-dicarboxylate (16a): This compound was synthesized according to General Procedure 1; **15a** (1.23 g, 4.02 mmol),[37] after photolysis in benzene (150 mL) at 18 °C for 28 min and recrystallization (methanol), yielded **16a** (0.72 g, 2.57 mmol, 64%) as colourless crystals, m.p. 83−84 °C. − IR (KBr): $\tilde{\nu}$ = 3100−2800, 1712, 1625 cm^{-1}. − ^{1}H NMR [250 MHz, Eu(fod)$_3$ in $CDCl_3$]: δ = 1.21 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.90 (dd, ^3J = 8.0, ^4J = 0.9 Hz, 1 H, 4-H), 1.98 (d, ^3J = 8.0 Hz, 1 H, 2-H), 2.26 (d, ^3J = 3.7 Hz, 1 H, 7-H), 3.67 (s, 3 H, OCH_3), 3.70 (s, 3 H, CO_2CH_3), 7.96 (dd, ^3J = 3.7, ^4J = 0.9 Hz, 1 H, 6-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.7 (−CH_3, 1 C, 3-CH_3), 20.4 (−CH_3, 1 C, 8-CH_3), 22.3 (=CH, 1 C, C-4), 25.9 (=CH, 1 C, C-2), 26.4 (quat. C, 1 C, C-8), 26.7 (−CH_3, 1 C, 8-CH_3), 29.2 (=CH, 1 C, C-7), 31.8 (quat. C, 1 C, C-3), 32.2 (−CH_3, 1 C, 3-CH_3), 34.4 (quat. C, 1 C, C-1), 51.7 (−CH_3, 1 C, O*C*H_3), 52.1 (−CH_3, 1 C, O*C*H_3), 131.1 (quat. C, 1 C, C-5), 136.9 (=CH, 1 C, C-6), 167.4 (quat. C, 1 C, *C*O_2CH_3), 174.7 (quat. C, 1C, *C*O_2CH_3). − UV/Vis (CH_3OH): λ_{max} (ε) = 237 (6064). − MS (EI, 70 eV): *m*/*z* (%) = 278 (12) [M^+]. − $C_{16}H_{22}O_4$ (278.3): calcd. C 69.04, H 7.97; found C 69.05, H 7.82.

***cis*-1,5-Diphenyltricyclo[5.1.0.0^{2,4}]oct-5-ene (16c):** This compound was synthesized according to General Procedure 2; **15c** (65.2 mg, 0.190 mmol),[37] after photolysis (500 W/305-nm glass filter) in CH_3CN (25 mL) at room temp. for 75 min, yielded **16c** (59.0 mg, 0.190 mmol, quant.) as a yellow, glassy residue. − IR (KBr): $\tilde{\nu}$ = 3080, 3060, 3030, 2960, 2940, 2870, 2730, 1590, 1490, 1440, 1380, 1370, 1120, 1070, 1030, 1005, 930, 905, 870, 845, 755, 725, 690 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.35 (d, ^3J = 8.3 Hz, 1 H, 2-H), 1.43 (dd, ^3J = 8.3, ^4J = 0.7 Hz, 1 H, 4-H), 1.63 (d, ^3J = 3.9 Hz, 1 H, 7-H), 6.62 (dd, ^3J = 3.9, ^4J = 0.7 Hz, 1 H, 6-H), 7.13−7.55 (m, 10 H, Ar-H). − MS (EI, 70 eV): *m*/*z* (%) = 314 (75) [M^+].

***cis*-1,5-Bis(2-methyl-1,3,4-oxadiazol-5-yl)tricyclo[5.1.0.0^{2,4}]oct-5-ene (16d):** This compound was synthesized according to General Procedure 2; compound **15d** (2.02 g; 5.70 mmol),[37] after photolysis (200 W/360-nm glass filter) in CH_3CN (45 mL) at 18 °C for 43 h and purification by FC (CH_2Cl_2/EtOA*c* = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **16d** (1.40 g, 4.28 mmol, 75%) as colourless crystals, m.p. 115−116 °C. − IR (KBr): $\tilde{\nu}$ = 2990, 2950, 2920, 1620, 1570, 1550, 1520, 1230, 1200, 1185, 1110, 1070, 1010, 965, 945, 720 cm^{-1}. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.02 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.49 (d, ^3J = 8.1 Hz, 1 H, 2-H), 1.74 (ddd, ^3J = 8.1, ^4J = 1.1, ^5J = 1.0 Hz, 1 H, 4-H), 2.18 (dd, ^3J = 3.9, ^5J = 1.0 Hz, 1 H, 7-H), 2.51 (s, 3 H, Ar-CH_3), 2.52 (s, 3 H, Ar-CH_3), 7.02 (dd, ^3J = 3.9, ^4J = 1.1 Hz, 1 H, 6-H). − ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 11.3 (−CH_3, 1 C, Ar-*C*H_3), 11.3 (−CH_3, 1 C, Ar-*C*H_3), 19.9 (−CH_3, 1 C, 3-CH_3), 20.1 (−CH_3, 1 C, 8-CH_3), 22.1 (=CH, 1 C, C-4), 25.0 (quat. C, 1 C, C-8), 27.1 (−CH_3, 1 C, 8-CH_3), 27.2 (=CH, 1 C, C-2), 27.7 (quat. C, 1C, C-3), 29.5 (=CH, 1 C, C-7), 32.2 (−CH_3, 1 C, 3-CH_3), 32.5 (quat. C, 1 C, C-1), 125.6 (quat. C, 1 C, C-5), 130.3 (=CH, 1 C, C-6), 163.6 (quat. C, 1 C, Ar-C), 164.2 (quat. C, 1 C, Ar-C), 165.7 (quat. C, 1 C, Ar-C), 170.8 (quat. C, 1 C, Ar-C). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 256 (13800). − MS (EI, 70 eV): *m*/*z* (%) = 326 (13) [M^+]. − $C_{18}H_{22}N_4O_2$ (326.4): calcd. C 66.24, H 6.79, N 17.17; found C 65.95, H 6.85, N 16.95.

***cis*-1,5-Bis(2-pyridyl)tricyclo[5.1.0.0^{2,4}]oct-5-ene (16f):** This compound was synthesized according to General Procedure 2; com-

pound **15f** (303 mg, 0.880 mmol),[37] after photolysis (500 W/360-nm glass filter) in CH_3CN (45 mL) at room temp. for 36 h and purification by FC [CH_2Cl_2/PE/EtOH, 10:2:1] and recrystallization [Et_2O/PE] at −22 °C, yielded **16f** (150 mg, 0.474 mmol, 54%) as a colourless, amorphous powder, m.p. 98−99 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3010, 2960, 2930, 2870, 1580, 1560, 1465, 1425, 1370, 1145, 775, 740 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.44 (d, ^3J = 8.2 Hz, 1 H, 2-H), 1.54 (dd, ^3J = 8.2, ^4J = 0.9 Hz, 1 H, 4-H), 1.92 (d, ^3J = 3.9 Hz, 1 H, 7-H), 7.38 (dd, ^3J = 3.9, ^4J = 0.9 Hz, 1 H, 6-H) 7.08−7.12 (m, 2 H, Ar-H), 7.22−7.24 (m, 1 H, Ar-H), 7.32−7.35 (m, 1 H, Ar-H), 7.58−7.62 (m, 1 H, Ar-H), 7.65−7.70 (m, 1 H, Ar-H), 8.60−8.62 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (−CH_3, 1 C, 3-CH_3), 20.8 (−CH_3, 1 C, 8-CH_3), 24.2 (=CH, 1 C, C-4), 26.8 (quat. C, 1 C, C-8), 28.9 (−CH_3, 1 C, 8-CH_3), 30.1 (=CH, 1 C, C-2), 30.2 (quat. C, 1 C, C-3), 31.1 (=CH, 1 C, C-7), 32.5 (−CH_3, 1 C, 3-CH_3), 35.2 (quat. C, 1 C, C-1), 120.4 (=CH, 1 C, Ar-C), 120.7 (=CH, 1 C, Ar-C), 121.8 (=CH, 1 C, Ar-C), 122.7 (=CH, 1 C, C-6), 126.8 (=CH, 1 C, Ar-C), 136.4 (=CH, 1C, Ar-C), 136.5 (=CH, 1 C, Ar-C), 137.4 (quat. C, 1 C, C-5), 149.1 (=CH, 1 C, Ar-C), 149.3 (=CH, 1 C, Ar-C), 157.2 (quat. C, 1 C, Ar-C), 167.4 (quat. C, 1 C, Ar-C). − UV/Vis (CH_3CN): λ_{max} (ε) = 228 (11900), 262 (12700), 291 (10000). − $C_{22}H_{24}N_2$ (316.4): calcd. C 83.50, H 7.64, N 8.85; found C 83.27, H 7.84, N 8.85.

Dimethyl *trans*-Tricyclo[5.1.0.0^{2,4}]oct-5-ene-1,5-dicarboxylate (17a): This compound was synthesized according to General Procedure 2; compound **15a** (0.60 g; 1.96 mmol)[37] was photolysed (500 W/280-nm glass filter) under sensitized conditions in acetone (38 mL, sensitizer) at 18 °C for 7 h. The solvent was removed under reduced pressure and the residue was purified by FC (CH_2Cl_2) to afford **17a** (125 mg, 0.45 mmol, 23%) as a colourless oil. − IR (film): $\tilde{\nu}$ = 1720 cm^{-1}. − ^1H NMR [90 MHz, Eu(fod)$_3$ in $CDCl_3$]: δ = 1.24 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 1.86 (d, ^3J = 8.9 Hz, 1 H, 4-H), 2.13 (d, ^3J = 8.9 Hz, 1 H, 2-H), 2.38 (d, ^3J = 5.5 Hz, 1 H, 7-H), 3.73 (s, 3 H, -OCH_3), 3.74 (s, 3 H, -OCH_3), 7.74 (d, ^3J = 5.5 Hz, 1 H, 6-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 15.1 (−CH_3, 1 C, 3-CH_3), 17.2 (−CH_3, 1 C, 8-CH_3), 21.8 (−CH_3, 1 C, 8-CH_3), 24.8 (=CH, 1 C, C-2), 24.9 (=CH, 1 C, C-4), 25.2 (quat. C, 1 C, C-3), 27.4 (−CH_3, 1 C, 3-CH_3), 30.6 (=CH, 1 C, C-7), 35.0 (quat. C, 1 C, C-1), 36.1 (quat. C, 1 C, C-8), 51.8 (−CH_3, 1 C, OCH_3), 51.8 (−CH_3, 1 C, OCH_3), 127.5 (quat. C, 1 C, C-5), 134.2 (=CH, 1 C, C-6), 167.4 (s, quat. C, 1 C, CO_2CH_3), 173.7 (quat. C, 1 C, CO_2CH_3). − UV/Vis (CH_3OH): λ_{max} (ε) = 259 (6350). − MS (HR): calcd: 278.1518, found 278.1515.

1,5-Dicyano-*trans*-tricyclo[5.1.0.0^{2,4}]oct-5-ene (17b): This compound was synthesized according to General Procedure 2; compound **15b** (0.36 g, 1.50 mmol),[37] after sensitized photolysis (500 W/280-nm glass filter) in acetone (38 mL, sensitizer) at room temp. for 2.5 h and recrystallization [CH_2Cl_2/PE], yielded **17b** (0.165 g, 0.780 mmol, 52%) as colourless crystals, m.p. 97−100 °C. − IR (KBr): $\tilde{\nu}$ = 2240, 2220 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 1.20 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.25 (d, ^3J = 8.8 Hz, 1 H, 2-H), 1.42 (d, ^3J = 8.8 Hz, 1 H, 4-H), 1.61 (d, ^3J = 5.3 Hz, 1 H, 7-H), 6.48 (d, ^3J = 5.3 Hz, 1 H, 6-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 14.9 (−CH_3, 1 C, 3-CH_3), 15.6 (−CH_3, 1 C, 8-CH_3), 21.1 (quat. C, 1 C), 23.6 (=CH, 1 C), 25.0 (−CH_3, 1 C, 8-CH_3), 25.5 (=CH, 1 C), 26.9 (−CH_3, 1 C, 3-CH_3), 27.3 (quat. C, 1 C), 31.5 (=CH, 1 C, C-7), 35.4 (quat. C, 1 C, C-8), 110.0 (quat. C, 1 C), 118.6 (quat. C, 1 C), 121.0 (quat. C, 1 C), 137.1 (=CH, 1 C, C-6). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 250 (6350). − MS (HR): calcd: 212.1313; found 212.1302. − $C_{14}H_{16}N_2$ (212.1): calcd. C 79.19, H 7.61, N 13.20; found C 79.03, H 7.46, N 13.04.

***trans*-1,5-Bis(2-methyl-1,3,4-oxadiazol-5-yl)tricyclo[5.1.0.0^{2,4}]oct-5-ene (17d):** This compound was synthesized according to General Procedure 2; compound **16d** (106 mg, 0.325 mmol), after sensitized photolysis (200 W/295-nm glass filter) in acetone (30 mL, sensitizer) at 18 °C for 3.5 h and purification by FC (CH_2Cl_2/EtOAc, 1:1), yielded **17d** (89.0 mg, 0.273 mmol, 84%) as a colourless oil. − IR (KBr): $\tilde{\nu}$ = 3040, 2940, 2915, 2860, 1630, 1570, 1550, 1520, 1440, 1365, 1325, 1230, 1210, 1010, 960, 945, 720 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.69 (d, ^3J = 8.7 Hz, 1 H, 2-H), 1.78 (d, ^3J = 8.7 Hz, 1 H, 4-H), 2.16 (d, ^3J = 5.5 Hz, 1 H, 7-H), 2.54 (s, 3H, Ar-CH_3), 2.55 (s, 3H, Ar-CH_3), 6.71 (d, ^3J = 5.5 Hz, 1 H, 6-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 11.0 (−CH_3, 2 C, Ar-CH_3), 15.1 (−CH_3, 1 C, 3-CH_3), 16.7 (−CH_3, 1 C, 8-CH_3), 22.5 (−CH_3, 1 C, 8-CH_3), 24.6 (=CH, 1 C, C-2), 24.7 (=CH, 1 C, C-4), 25.9 (quat. C, 1 C, C-3), 27.3 (−CH_3, 1 C, 3-CH_3), 27.7 (quat. C, 1 C, C-1), 29.9 (=CH, 1 C, C-7), 35.9 (quat. C, 1 C, C-8), 120.9 (quat. C, 1 C, C-5), 127.2 (=CH, 1 C, C-6), 163.0 (quat. C, 1 C, Ar-C), 163.2 (quat. C, 1 C, Ar-C), 165.1 (quat. C, 1 C, Ar-C), 168.4 (quat. C, 1 C, Ar-C). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 269 (10600). − MS (EI, 70 eV): *m*/*z* (%) = 326 (15) [M^+]. − $C_{18}H_{22}N_4O_2$ (326.4): calcd. C 66.24, H 6.79, N 17.17; found C 65.81, H 6.94, N 16.91.

Dimethyl 5,5,8,8-Tetramethyl-1,3,6-cyclooctatriene-2,6-dicarboxylate (18a): Compound **16a** (47.9 mg, 0.172 mmol) was dissolved in CH_3CN (5 mL) and heated under reflux for 12 h. The resulting product **18a** (47.8 mg, 0.172 mmol, quant.) was isolated as a colourless oil. − IR (KBr): $\tilde{\nu}$ = 3100−2800, 1720, 1650−1600 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.30 (s, 6 H, CH_3), 1.32 (s, 6 H, CH_3), 3.73 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 5.58 (d, ^3J = 11.3 Hz, 1 H, 7-H), 5.74 (d, ^4J = 0.6 Hz, 1 H, 2-H), 6.30 (dd, ^3J = 11.3, ^4J = 0.9 Hz, 1 H, 6-H), 6.62 (dd, ^4J = 0.9, ^4J = 0.6 Hz, 1 H, 4-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.5 (−CH_3, 2 C, 8-CH_3), 30.5 (−CH_3, 2 C, 3-CH_3), 37.8 (quat. C, 1 C, C-3), 38.3 (quat. C, 1 C, C-8), 51.6 (−CH_3, 1 C, OCH_3), 52.0 (−CH_3, 1 C, OCH_3), 126.1 (=CH, 1 C, C-6), 132.7 (quat. C, 1 C, C-5), 140.4 (quat. C, 1 C, C-1), 141.6 (=CH, 1 C, C-7 or C-4), 141.8 (=CH, 1 C, C-4 or C-7), 148.9 (=CH, 1 C, C-2), 167.3 (quat. C, 1 C, CO_2CH_3), 171.6 (quat. C, 1 C, CO_2CH_3). − UV/Vis (CH_3OH): λ_{max} (ε) = 225 (6819). − MS (EI, 70 eV): *m*/*z* (%) = 278 (7) [M^+]. − $C_{16}H_{22}O_4$ (278.3): calcd. C 66.24, H 6.79, N 17.17; found C 65.81, H 6.94, N 16.91.

2,6-Dicyano-5,5,8,8-tetramethyl-1,3,6-cyclooctatriene (18b): Compound **15b** (0.13 g, 0.541 mmol),[37] after thermolysis at 250 °C for 10 min, purification by FC (CH_2Cl_2) and recrystallization [CH_2Cl_2/PE], yielded **18b** (35 mg, 0.165 mmol, 30%) as colourless crystals, m.p. 91−96 °C. − IR (KBr): $\tilde{\nu}$ = 2215 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.35 (s, 6 H, CH_3), 1.45 (s, 6 H, CH_3), 5.68 (d, ^3J = 11.2 Hz, 1 H, 7-H), 6.09 (dd, ^3J = 11.2, ^4J = 1.0 Hz, 1 H, 6-H), 6.23 (br. s, ^4J = 1.0 Hz, 1 H, 4-H), 6.31 (d, ^4J = 0.6 Hz, 1 H, 2-H). − MS (HR): calcd: 212.1313; found 212.1313.

5,5,8,8-Tetramethyl-2,6-diphenyl-1,3,6-cyclooctatriene (18c): Compound **16c** (55.3 mg, 0.176 mmol), after thermolysis at 240 °C for 30 min and without further purification, yielded **18c** (53 mg, 0.17 mmol, 96%) as a yellow oil. − IR (KBr): $\tilde{\nu}$ = 3070, 3050, 3020, 2990, 2950, 2900, 2860, 1595, 1485, 1475, 1455, 1440, 1355, 1255, 1170, 1070, 1025, 855, 770, 755, 740, 690 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.14 (s, 6 H, CH_3), 1.35 (s, 6 H, CH_3),

5.34 (br. s, 1 H, 2-H), 5.70 (d, ^3J = 11.3 Hz, 1 H, 7-H), 5.87 (br. s, ^4J = 0.5 Hz, 1 H, 4-H), 6.26 (dd, ^3J = 11.3, ^4J = 0.5 Hz, 1 H, 6-H), 7.08−7.49 (m, 10 H, Ar-H). − MS (EI, 70 eV): *m*/*z* (%) = 315 (14) [M^+].

5,5,8,8-Tetramethyl-2,6-bis(2-methyl-1,3,4-oxadiazol-5-yl)-1,3,6-cyclooctatriene (18d): A solution of compound **16d** (15.4 mg, 0.048 mmol) in CH_3CN (3 mL) was stirred at 60 °C for 8 h, and after recrystallization (CH_2Cl_2/*n*-hexane) yielded **18d** (12.2 mg, 0.037 mmol, 78%) as colourless crystals, m.p. 146 °C. − IR (KBr): $\tilde{\nu}$ = 2970, 2940, 2910, 2850, 1560, 1530, 1515, 1420, 1300, 1205, 955, 885, 855, 810, 700 cm^{-1}. − ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.27 (s, 6 H, CH_3), 1.41 (s, 6 H, CH_3), 2.49 (s, 3H, Ar-CH_3), 2.52 (s, 3H, Ar-CH_3), 5.78 (d, ^3J = 11.3 Hz, 1 H, 7-H), 6.01 (d, ^4J = 0.6 Hz, 1 H, 2-H), 6.43 (dd, ^4J = 0.6, ^4J = 0.9 Hz, 1 H, 4-H), 6.46 (dd, ^3J = 11.3, ^4J = 0.6 Hz, 1 H, 6-H). − ^{13}C NMR (400 MHz, CD_2Cl_2): δ = 11.2 (−CH_3, 2 C, Ar-*C*H_3), 29.6 (−CH_3, 2 C, 8-CH_3), 30.0 (br. s, −CH_3, 2 C, 3-CH_3), 38.7 (quat. C, 1 C, C-3), 39.5 (quat. C, 1 C, C-8), 125.3 (=CH, 1 C, C-6), 126.5 (quat. C, 1 C, C-5), 132.1 (quat. C, 1 C, C-1), 142.9 (=CH, 2 C, C-7, C-4), 147.8 (=CH, 1 C, C-2), 163.5 (quat. C, 1 C, Ar-C), 163.9 (quat. C, 1 C, Ar-C), 164.8 (quat. C, 1 C, Ar-C), 167.9 (quat. C, 1 C, Ar-C). − UV/Vis (CH_3CN): λ_{max} (ε) = 242 (13200). − MS (EI, 70 eV): *m*/*z* (%) = 326 (9) [M^+]. − $C_{18}H_{22}N_4O_2$ (326.4): calcd. C 66.24, H 6.79, N 17.17; found C 66.07, H 6.76, N 16.91.

5,5,8,8-Tetramethyl-2,6-bis(2-thiazolyl)-1,3,6-cyclooctatriene (18e): This compound was synthesized according to General Procedure 2; compound **15e** (390 mg, 1.09 mmol),[37] after photolysis (500 W/360-nm glass filter) in CH_3CN (30 mL) at 18 °C for 75 h and purification by FC [CH_2Cl_2/PE/EtOH, 15:2:1], gave **18e** (293 mg, 0.890 mmol, 82%) as a yellow oil instead of the expected *cis*-1,5-bis(2-thiazolyl)tricyclo[5.1.0.0^{2,4}]oct-5-ene (**16e**). − IR (KBr): $\tilde{\nu}$ = 3100, 3070, 2990, 2950, 2920, 2860, 1600, 1475, 1450, 1405, 1360, 1350, 1215, 1130, 1045, 900, 855, 800, 720 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 6 H, CH_3), 1.41 (s, 6 H, CH_3), 5.79 (br. s, 1 H, 4-H), 5.83 (d, ^3J = 11.4 Hz, 1 H, 7-H), 6.47 (br. s, 1 H, 2-H), 6.49 (d, ^3J = 11.4 Hz, 1 H, 6-H), 7.21 (d, ^3J = 3.4 Hz, 1 H, Ar-H), 7.27 (d, ^3J = 3.3 Hz, 1 H, Ar-H), 7.71 (d, ^3J = 3.4 Hz, 1 H, Ar-H), 7.81 (d, ^3J = 3.3 Hz, 1 H, Ar-H). − MS (EI, 70 eV): *m*/*z* (%) = 328 (7) [M^+].

5,5,8,8-Tetramethyl-2,6-bis(2-pyridyl)-1,3,6-cyclooctatriene (18f): Compound **16f** (200 mg, 0.632 mmol), after thermolysis at 280 °C for 10 min, purification by FC (CH_2Cl_2/*n*-hexane/EtOH, 10:2:1) and recrystallization (Et_2O/*n*-hexane), yielded **18f** (59.9 mg, 0.191 mmol, 30%) as colourless crystals, m.p. 97−98 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 3040, 2990, 2950, 2920, 2900, 2860, 1605, 1575, 1550, 1460, 1420, 1365, 1350, 1255, 1220, 1140, 985, 860, 785, 765, 745, 735 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 5.43 (br. s, 1 H, 4-H), 5.80 (d, ^3J = 11.2 Hz, 1 H, 7-H), 6.45 (d, ^3J = 11.2 Hz, 1 H, 6-H), 6.58 (br. s, 1 H, 2-H), 7.09−7.17 (m, 3 H, Ar-H), 7.41−7.43 (m, 1 H, Ar-H), 7.58−7.67 (m, 2 H, Ar-H), 8.52−8.54 (m, 1 H, Ar-H), 8.61−8.63 (m, 1 H, Ar-H). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 227 (17400), 255 (12700), 281 (9190). − $C_{22}H_{24}N_2$ (316.4): calcd. C 83.50, H 7.64, N 8.85; found C 83.50, H 7.58, N 8.81.

Conversion of Dimethyl *cis*-Tricyclo[5.1.0.0^{2,4}]oct-5-ene-1,5-dicarboxylate (16a) into Dimethyl *trans*-Tricyclo[5.1.0.0^{2,4}]oct-5-ene-1,5-dicarboxylate (17a): This transformation was carried out according to General Procedure 2; compound **16a** (100 mg, 0.360 mmol), after sensitized photolysis (500 W/280-nm glass filter) in acetone (38 mL, sensitizer) at room temp. for 5 h, yielded one single product (75 mg, 0.270 mmol, 75%), which was identical with a sample of **17a** by HPLC and ^1H NMR analysis

Conversion of Dimethyl 5,5,8,8-Tetramethyl-1,3,6-cyclooctatriene-2,6-dicarboxylate (18a) into Dimethyl *trans*-Tricyclo[5.1.0.0^{2,4}]oct-5-ene-1,5-dicarboxylate (17a): This transformation was carried out according to General Procedure 2; compound **18a** (7.8 mg, 0.03 mmol), after sensitized photolysis (500 W/280-nm glass filter) in acetone (4 mL, sensitizer) at room temp. for 2 h, yielded one single product (5.3 mg, 0.02 mmol, 68%), which was identical with a sample of **17a** by HPLC analysis.

Conversion of 2,6-Dicyano-5,5,8,8-tetramethyl-1,3,6-cyclooctatriene (18b) into 1,5-Dicyano-*trans*-tricyclo[5.1.0.0^{2,4}]oct-5-ene (17b): This transformation was carried out according to General Procedure 2; compound **18b** (18 mg, 0.08 mmol), after sensitized photolysis (500 W/280-nm glass filter) in acetone (2 mL, sensitizer) at room temp. for 30 min, yielded one single product (13.9 mg, 0.07 mmol, 77%), which was identical with a sample of **17b** by HPLC analysis.

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