Azo Bridges from Azines, XXIII[◇]

1,5-Laticyclic Conjugation Between Parallel Azo and *o*-Phenylene Bridges. Structure Dependence of [6 + 2] Photocycloadditions☆

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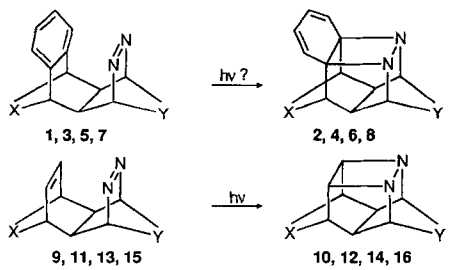
Examples were synthesized of the four systems **1**, **3**, **5**, and **7**, in which rigid parallelo *o*-phenylene and azo bridges are connected to five- and/or six-membered carbocyclic moities. The *o*-phenylene bridge was introduced by two routes: (A) starting from precursors already containing that bridge (**24**, **29**) and assembling the azo bridge in consecutive steps (→ **3a**, **3b**, **5c**, **5d**, **5e**, **5f**, **5g**); (B) starting from the systems with parallel C=C/N=N bridges (**9a**, **11a**, **13a**, **42**) and completing the dihydro-*o*-phenylene ring by tetrachlorothiophene dioxide. Dyotropic hydrogen transfer of the azo bridge enhances the dehydrogenation of the intermediate dihydro-*o*-phenylene derivatives (**22**, **3cH$_2$**, **25**). This mechanism was proved by the domino hydrogen transfer **44** → **45** → **5h**. Via route B, systems **1a**, **1b**, **3c**, **3d**, **5a**, **5b**, **5h**, and **43** were obtained. In sharp contrast to the smooth [2 + 2] photocycloaddition of systems **9**, **11**, **13**, and **15** (C=C/N=N bridges), [6 + 2] photocycloaddition occurs only with systems **1** and ($5_C/5_N$) and **3** ($6_C/5_N$) but not with systems **5** ($5_C/6_N$) and **7** ($6_C/6_N$). These differences are not caused by slightly varying distances of the two bridges (X-ray data) but by the higher n_- ionization energy of the azo group incorporated into a 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) instead of a 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) moiety, the hypsochromicity of the corresponding DBH n-π* state and the higher ground-state energy of DBH compared to DBO.

In several papers of this series, compounds of type **9**, **11**, **13**, and **15** with parallel double bonds and azo groups have been demonstrated to yield cleanly [2 + 2] cycloaddition products of type **10**, **12**, **14**, and **16** by n-π* photoexcitation of the azo group. These [$\pi_S^2+\pi_S^2$] reactions proceed smoothly without denitrogenation, irrespective of the size of the carbocyclic rings which carry the bridging C=C and N=N bonds: **10** ($5_C/5_N$)[4,5,6], **12** ($6_C/5_N$)[7], **14** ($5_C/6_N$)[4] and **16** ($6_C/6_N$)[4].

These encouraging results prompted us to replace the vinylene bridge by an *o*-phenylene moiety, thus creating types **1**, **3**, **5**, and **7**. We wondered if a 1,5-laticyclic conjugation could be observed, possibly even a [6 + 2] photocycloaddition to types **2**, **4**, **6**, and **8** a reaction which, however, may be rather sensitive to the size of the rings carrying the two bridges.

We now report on the synthesis of several examples representing types **1**, **3**, **5**, and **7** and the structural prerequisites allowing [$\pi_S^6 + \pi_S^2$] photocycloadditions.



Type		X/Y
1,2	9,10	$5_C/5_N$
3,4	11,12	$6_C/5_N$
5,6	13,14	$5_C/6_N$
7,8	15,16	$6_C/6_N$

Fragments X and Y complete five or six membered rings with an unsaturated (5_C, 6_C) or azo bridge (5_N, 6_N).

1. Synthesis of Types 1, 3, 5, and 7

Systems of types **1**, **3**, **5**, and **7** were approached by one of the following two routes:

A. Ultimate introduction of the azo bridge by [4 + 2] cycloaddition of appropriate azines with olefins already carrying an *o*-phenylene bridge according to the basic reaction employed previously in this series of papers.

[◇] Part XXII. Ref.[1].

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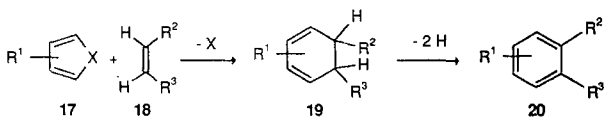
B. Ultimate introduction of the *o*-phenylene bridge by transformation of bridging double bonds into aromatic rings according to the following scheme.

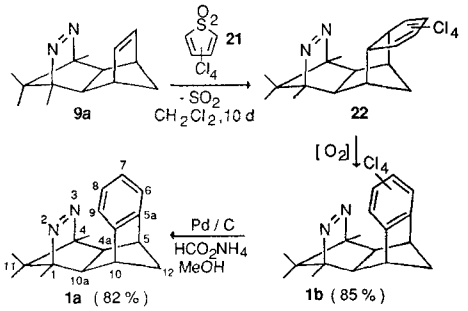


17 18 19 20

Dienes **17** first form a [4 + 2] cycloaddition adduct with **18** from which group X is extruded by a chelotropic reaction. Subsequent dehydrogenation of **19** finally yields the aromatic system **20**. For **17** mainly tetrachloro cyclopentadiene[8] or its dimethyl ketale[9], α-pyrone[10], and tetrachlorothiophenedioxide (**21**)[11] have been applied. We concentrated on **21**, a highly reactive but persistent dienophile[11].

1.1. Synthesis of System 1 ($5_C/5_N$)

The crucial precursor **1b** is easily obtained by reacting compound **9a**[12] with **21**. On chromatography of the reaction mixture only small amounts of the initial product **22** can be detected since **22** is very easily dehydrogenated to **1b** by air (*vide infra*). Catalytic dehydrochlorination[13] is smoothly accomplished to the expected phenylene derivative **1a** without noticeable side products.



9a 22 1a (82%) 1b (85%)

1.2. Synthesis of System 3 ($6_C/5_N$)

Two representative examples of system **3** ($6_C/5_N$) are available by an improved and extended version of our briefly published[14] Diels-Alder reaction with inverse electron demand between the trimeric isopyrazole **23**[15] and benzobarrelene (**24**). Although **11a** (30%) and **3a** (15%) are formed in rather low yields based on reacted **24**, this route constitutes the most convenient one for the target compounds.

Cycloaddition of **21** with **11a** immediately yields the dehydrogenated aromatic compound **3c** (64%). Hydrogenation of the double bond in **3a** as well as dehydrochlorination of **3c** require well-balanced conditions in contrast to the corresponding reactions discussed above. Both hydrogenation and dehydrochlorination products **3b** and **3d** are obtained in lower yields than usual, probably due to competing reductive cleavage of the azo group.

1.3. Synthesis of System 5 ($5_C/6_N$)

Completely analogous to **1a**, synthesis of example **5a** starts with our workhorse **13a**[15] and the dienophile **21**[11]. In this case, however, the reaction stops mainly at the level of cycloaddition with dihydroaromatic compound **25** (80–88%) which is accompanied only by minor amounts of the aromatic system **5b** (2–6%). Nearly quantitative dehydrogenation of **25** to **5b** is easily achieved by heating **25** in toluene in the presence of air. Dehydrochlorination of **5b** finally yields **5a** ($5_C/6_N$), in which the cyclopentene moiety has been hydrogenated additionally.

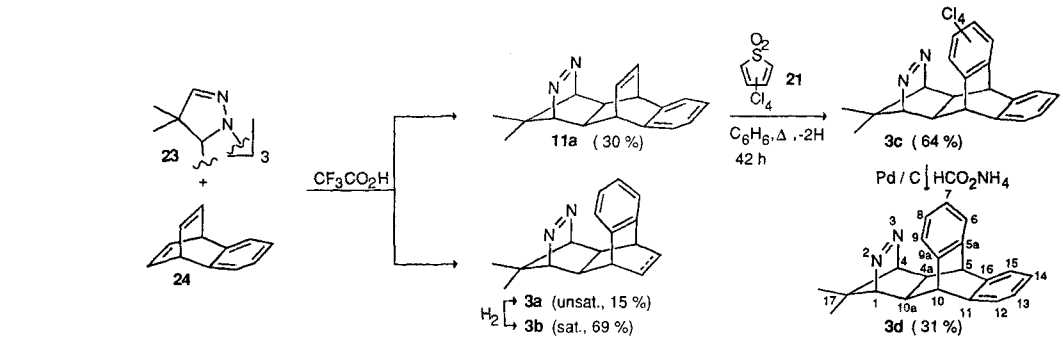
Starting with the azine route, we prepared the trimeric azine **29**[16] as the precursor for the acid-catalysed [4 + 2] cycloaddition with various olefins. To this end the known cyclic anhydride **26**[17] was quantitatively reduced to diol **27**. Swern oxidation of **27** to the hydrated dialdehyde **28** and subsequent reaction with hydrazine affords crude trimeric azine **29** which was directly subjected to the Diels–Alder reactions with inverse electron demand. Yields of cycloadducts are therefore based on diol **27**. As is to be expected from similar investigations[15,18] the dienophiles cyclopentadiene (**30**), norbornene (**32**), and norbornadiene (**34**) mainly yielded the expected *endo*-isomers **5c**, **5d**, and **5e** with parallel *o*-phenylene and azo bridges. The corresponding *exo*-isomers **31**, **33**, and **35** were detected in traces only. Compound **5c** is also available by the route discussed above through chemical reduction (Na, *t*-butanol, THF) of **33**, albeit in variable yields (22–66%)[3]. On the other hand, the saturated system **5a** should be easily accessible from **5c** by catalytic hydrogenation. Benzobarrelene (**24**) as dienophile principally follows the same reaction pattern. However, forced reaction conditions are needed and the two isomers **5f** and **15a** are formed in comparable yields. the olefinic bridge in **5f** is smoothly hydrogenated to form **5g**.

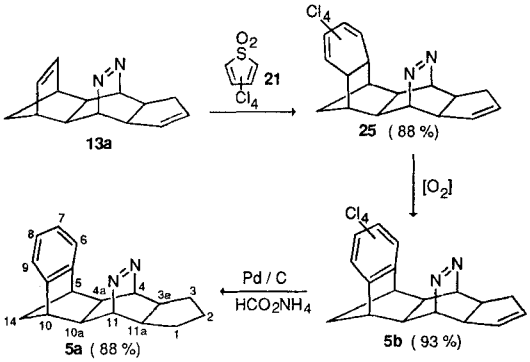
1.4. Synthesis of System 7 ($6_C/6_N$)

We terminated our approach to examples **7** ($6_C/6_N$) when Prinzbach[19] published compound **7a** prepared by the azine route together with its photochemistry (which will be discussed in section 3).

2. Intramolecular Dyotropic Hydrogen Transfer

As mentioned above, aromatization of Diels–Alder adducts obtained from tetrachlorothiophene dioxid (**21**) and several olefinic bridges occurs under remarkably mild conditions and in some cases the aromatic system is isolated directly. Obviously, the parallel azo group plays an important role, allowing principally dyotropic[20] transfer of the two hydrogen atoms from the cyclohexadiene unit (e.g. in **22** and **25**) to the azo group in a symmetry-allowed pericyclic reaction[21]. The hydrazo bridge thus formed is easily dehydrogenated by air in a consecutive step. Indeed, with system **36**[22] hydrogen is obviously transferred even from an ethano bridge to the azo group, albeit at rather high tem-





peratures. This isomerization can be concluded from the isolated product **38** which was supposed to be formed via **37** and **39**. The intermediate hydrazine **39** could even be trapped by succinic acid anhydride[22].

Intramolecular hydrogen transfer from a cyclohexadiene moiety to an etheno bridge has been observed with compound **40** which reacts to the stable iosmer **41**[23].

Recently, a mechanistic study (primary deuterium effects) of a number of similar systems has clearly demonstrated an intramolecular dyotropic reaction within certain geometrical limits[24].

The systems under consideration here allowed another variation of intramolecular hydrogen transfer, perhaps the first example for a domino or tandem[25] dyotropic reaction.

To this end, compound **42**[18], in which the azo bridge is flanked by two different vinylene bridges, is subjected to a [4 + 2] cycloaddition with **21** for 25 days at ambient temperature. As in other reactions of **42**[26] the norbornene moiety is preferentially attacked. Chromatography yields **44** (67%) and small amounts of **43** (8%).

On heating **44** in a toluene solution in the presence of air, its cyclohexadiene system is smoothly dehydrogenated to **43** (76%). If, however, **44** is heated under nitrogen, aromatization of the six-membered ring is accompanied by hydrogenation of the olefinic bridge and formation of **5h** (48%). This unprecedented reaction can only be explained by the intermediate hydrazine **45**. In this way, the two hydrogen atoms from the cyclohexadiene moiety are intramolecularly shifted to the vinylene unit. The latter reaction is suppressed on oxygen due to a faster dehydrogenation of the hydrazino bridge in **45**.

3. [6+2] Photocycloaddition

Similar to the rapid and smooth $[\pi_S^2+\pi_S^2]$ photocycloadditions of types **9**, **11**, **13**, **14**, and **10**[4-7], compounds **1a** and **1b** [type **1** ($5_C/5_N$)] easily undergo $[\pi_S^6/\pi_S^2]$ photocycloaddition, to **2a** and **2b** [type **2** ($5_C/5_N$)] respectively, when irradiated at $\lambda > 320$ nm. The same photoreaction is observed with **3a**, **3b**, and **3d** [type **3** ($6_C/5_N$)] which afford the cycloadducts **4a**, **4b**, and **4c** [type **4** ($6_C/5_N$)] under the same conditions.

In sharp contrast to this behaviour no photocycloaddition takes place in the related compounds **5c**, **5d**, and **5e** [type **5** ($5_C/6_N$)] and with **7a**[19] [type **7** ($6_C/6_N$)]. In particular, **7a** has been subjected to irradiation at different wavelengths and for different reaction times; however only the denitrogenation product **47** (λ = 250 nm, 2 d), ield up to 70% based on 60% conversion[19]) could be identified. Forced conditions were also applied to **5c**, whereby again slow decomposition occurred. The complex mixture could contain some **46**.

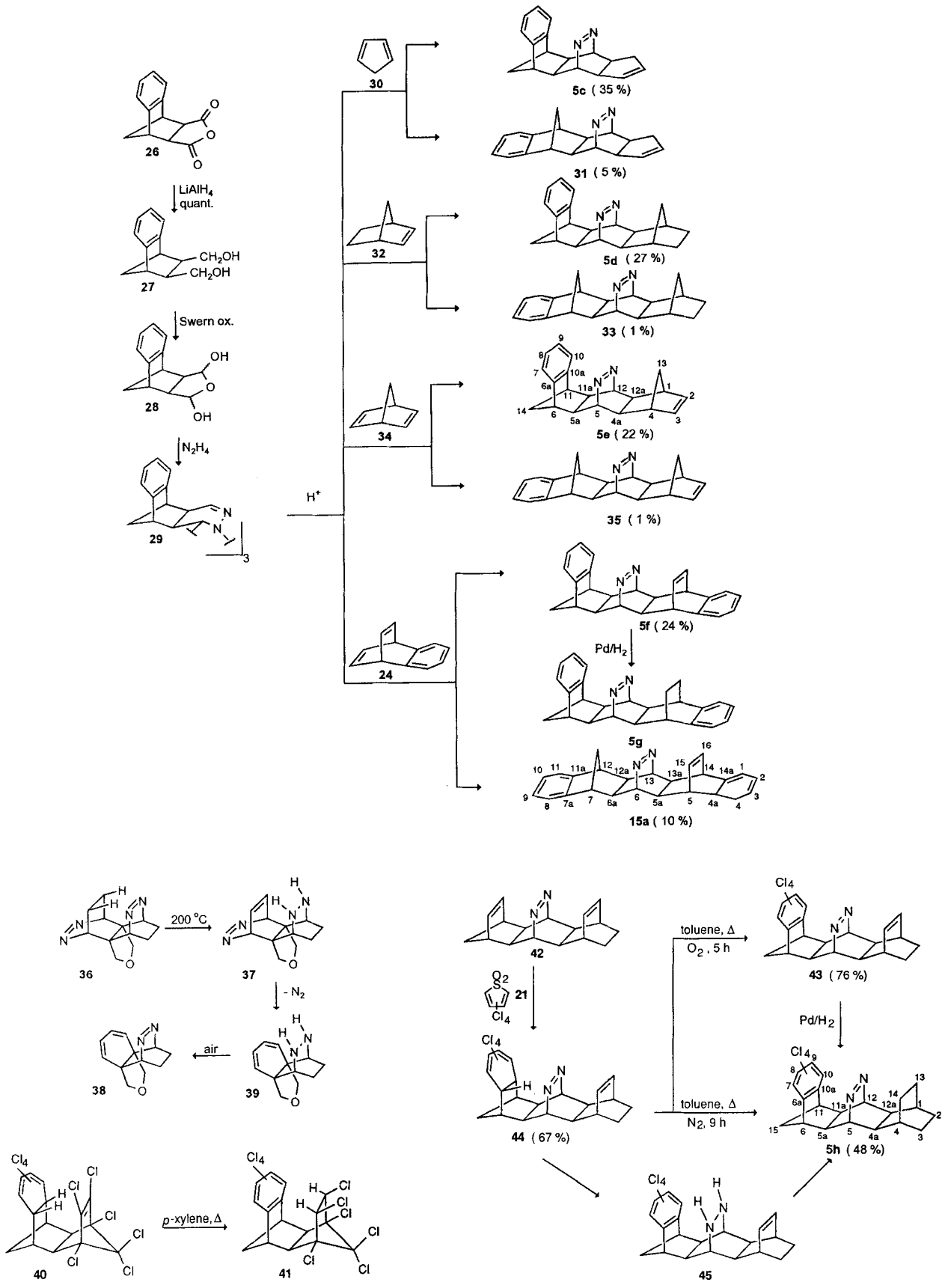
These experiments show very clearly that the expected [6+2] photocyclizations are restricted to systems **1** and **3** in which the azo group bridges a five-membered ring, whereas the neighbouring *o*-phenylene bridge may be anchored to either a five- or a six-membered ring. However, azo bridges positioned over a six-membered ring are not apt to undergo this [6+2] cycloaddition irrespective of the size of the ring carrying the *o*-phenylene bridge (systems **5** and **7**).

These puzzling results call for an explanation which may be found in the different geometries and energies of systems **1**, **3** and **5**, **7**, respectively.

4. Distances between the Bridging Elements in Systems 1, 3, 5 and 7

The crystal structure of compound **7a**, as a typical example of system **7** ($6_C/6_N$), has already been published[19]. We add X-ray structure determinations for **1a** (system **1**, $5_C/5_N$) and **3a** (system **5**, $5_C/6_N$), which confirm the presented formulae (Figures 1 and 2).

The critical data for a possible [6+2] photocycloaddition, viz. the distances between the bridging groups, are collected in Table 1. Calculated distances are reproduced best by MNDO, whereas HAM/3 (MM2) and MINDO/3 yield distances which are respectively too large and too small[26b,27] MNDO distances are too large by 11–12 pm. Conse-



quently for **5c**, for which a crystal structure is still missing, a distance of 291 nm can be estimated.

Interestingly, the corresponding systems **9a**, **13a**, and **42**, in which the *o*-phenylene bridge has been replaced by an

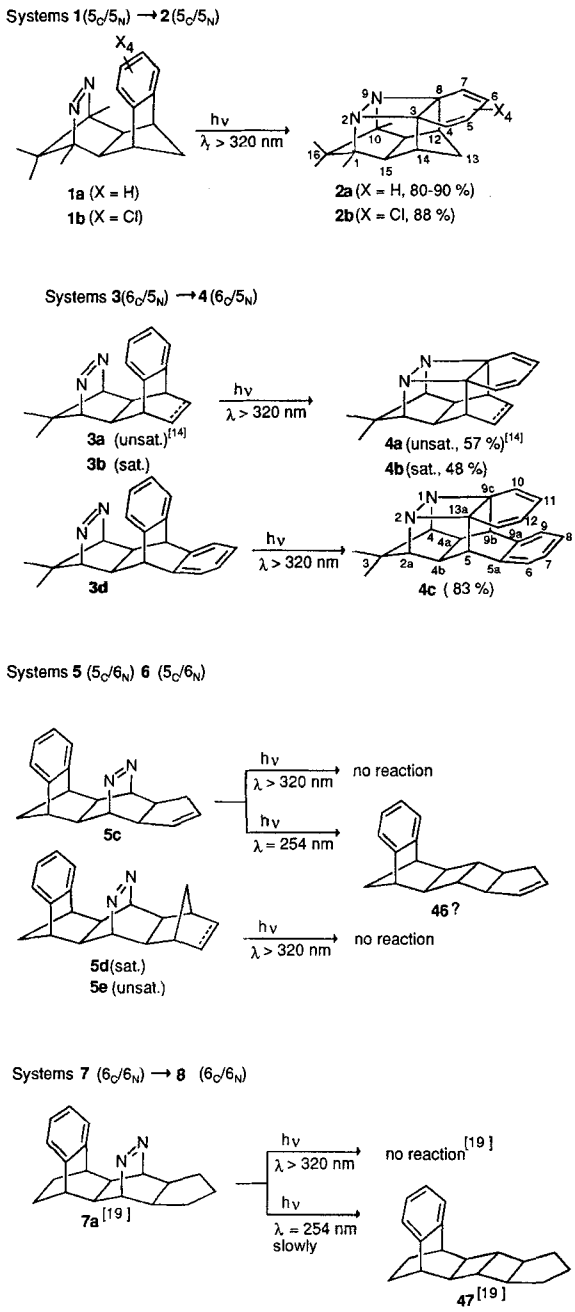


Figure 1. X-ray crystal structure of **1a**

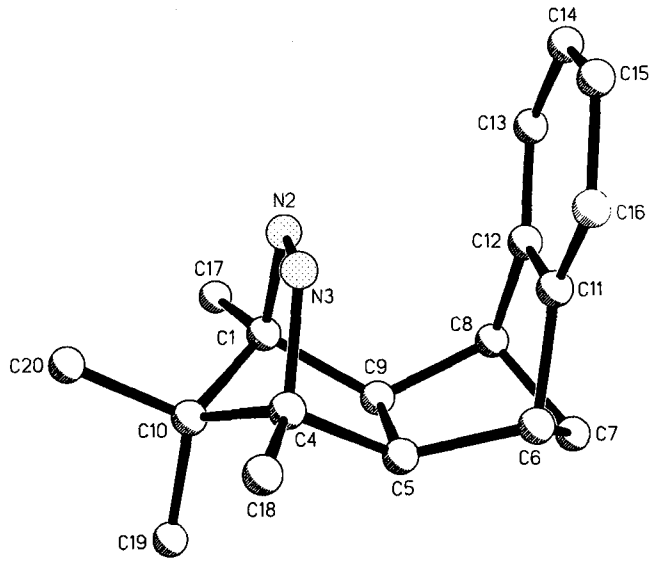
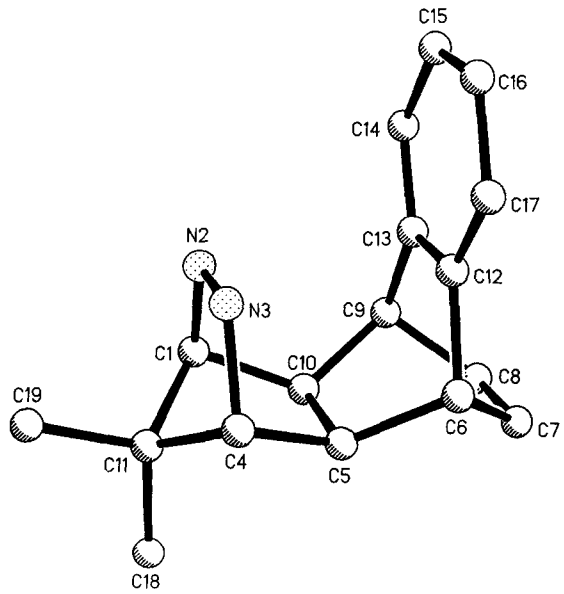


Figure 2. X-ray crystal structure of **3a**



olefinic one, exhibit the same distances between the bridges. From both **13a** and **42**, 291 pm is again estimated for **5c** (system **5**, $5_C/6_N$). The distance in the $6_C/6_N$ arrangement of **42** also agrees well with that reported for **7a** from X-ray data[19].

5. The n-π* Transitions of the Azo Bridges in Systems 1, 3, 5 and 7

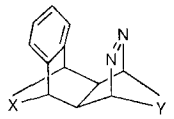
Within this series the n-π* transition of azo bridges in a close parallel position to a bridging olefinic group has already been thoroughly investigated and discussed[14,15,18,26b]. Consequently, the UV spectra of systems **1**, **3**, **5**, and **7** were measured and data for the n-π* transitions are collected in Table 2. As far as available, the corresponding data for the same systems with an olefinic instead of an *o*-phenylene bridge are also included in Table 2.

As one can easily see, the n-π* transitions of both systems are identical in the case of **1** ($5_C/5_N$) and **3** ($6_C/5_N$). With systems **5** ($5_C/6_N$), and **7** ($6_C/6_N$), however, the *o*-phenylene bridges cause the absorptions to move to shorter wavelength by 4–7 nm.

6. Photoelectron Spectra of Systems 3 and 5

Since orbital energies derived from photoelectron spectra may indicate the different behaviour of systems **1** and **5**, these data were collected for **3a** (system **3**, $6_C/5_N$)[28] together with **5c** and **5a** (system **5**, $5_C/6_N$). Compound **13a** ($5_C/6_N$, C=C instead of an *o*-phenylene bridge[26a]) has been included for comparison (Table 3).

Table 1. Distances [pm] between the azo and *o*-phenylene bridges in systems **1**, **3**, **5**, and **7** from X-ray data and MNDO calculations



1, 3, 5, 7

Type	Comp.	X-ray	Calc.
1 ($5_C/5_N$)	**1a**	280	--
3 ($6_C/5_N$)	**3a**	284	296
5 ($5_C/6_N$)	**5c**	(291)[a]	302
7 ($6_C/6_N$)	**7a**[19]	297[19]	308[19]

[a] Estimated, see text.

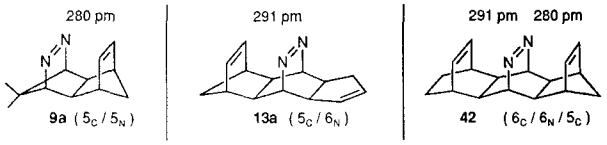
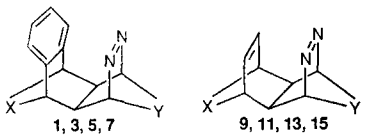


Table 2. UV maxima {$n \rightarrow \pi^*$, λ_{max} [nm] (ε)} in acetonitrile of azo compounds with neighbouring *o*-phenylene bridges compared with UV maxima {$n \rightarrow \pi^*$, λ_{max} [nm] (ε)} in hexane[a] of the corresponding compounds in which the *o*-phenylene bridge is replaced by an olefinic one (C=C)



1, 3, 5, 7 **9, 11, 13, 15**

Type	Comp.	nm (ε)	Comp.	nm (ε) [C=C]
1 or **9** ($5_C/5_N$)	**1a**	368 (498)	**9a**	369 (340)[15]
	1b	372 (653)		
3 or **11** ($6_C/5_N$)	**3a**	364 (641)		
		353 (189)		
	3b	360 (467)		
	3d	362 (497)	**11a**	363 (370)[14]
		352 (254)		353 (270)
5 or **13** ($5_C/6_N$)	**5a**	391 (185)	**13a**	395 (110)[18]
	5c	387 (186)	**13c**	394 (100), sh 384 (70), sh 355 (20)[26b]
	5d	390 (216)		
	5e	393 (181)	**13e**	sh 387 (65), sh 357 (20), 397 (105)[26b]
	5f	394 (243)		
	5g	380 (318)		
7 or **15** ($6_C/6_N$)	**7a**[19]	392 (145)	**15a**	397 (105), sh 387 (65), sh 357 (20)[26b]
		sh 381 195)		
		sh 353 (250)		

[a] According to several examples (cf. ref.[26b]) the absorption maxima in hexane and acetonitrile differ only by ca. 1 nm.

In an extension of earlier studies[27] the I_v data (Figure 3) could be assigned to the orbitals given in Table 3, backed by semi-empirical MINIDO/3 calculations[29]. In similar cases[27,30] these have proven to be more reliable than semi-empirical MNDO calculations[31].

Since **25** and **5a** differ only by one double bond in the cyclopentane moiety $I_{v,4}$(**3a**) = 9.1–9.2 eV can easily be assigned to π_{CC}Cy. The lowest ionization energy $I_{v,1}$ must be ascribed to the n_- orbital of the azo group. Its energy, $I_{v,1}$ = 7.9 eV, is not changed if the *o*-phenylene bridge is replaced by an olefinic one (**5c**, **5a** → **13a**) in systems with a 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) moiety, but is raised to $I_{v,1}$ = 8.15 eV in **3a** containing a 2,3-diazabicyclo-[2.2.1]hept-2-ene (DBH) unit (system **3**, $6_C/5_N$). In analogy with olefinic bridged systems[27] this difference of 0.25 eV is expected to be raised to 0.6–0.7 eV in systems $5_C/5_N$ reaching the difference between DBO and DBH itself[27]. Orbitals a'(π) and a''(π) arise from the benzene ring since their degeneracy is lost by the ortho substituents[32].

7. Discussions

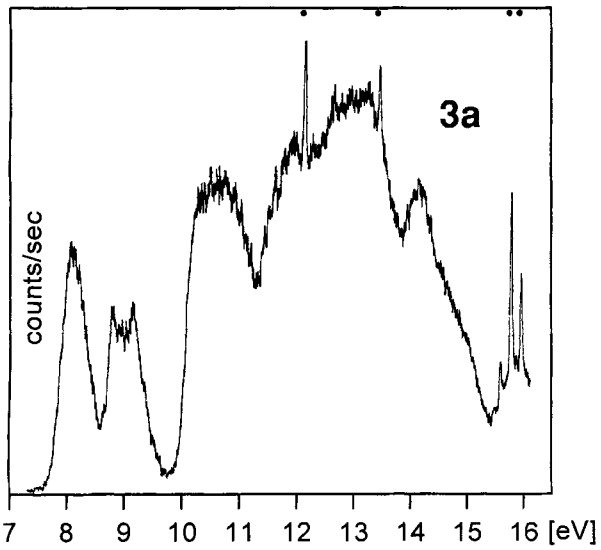
In an extension of already reported methods several examples of systems **1**, **3**, **5**, and **7** were synthesized. In these compounds *o*-phenylene and azo groups are held in rigid parallel position by bridging two connected five- and/or six-membered rings. In sharp contrast to systems with parallel C=C/N=N bridges of types **9**, **11**, **13**, and **15**, photocycloaddition between *o*-phenylene and azo bridges was only observed in systems of type **1** ($5_C/5_N$) and **3** ($6_C/5_N$) containing a DBH moiety and not with types **5** ($5_C/6_N$) and **7** ($6_C/6_N$) containing a DBO unit since the size of the ring which carries the *o*-phenylene bridge is unimportant. The main differences have to be sought in the azo-bridged part of the molecule.

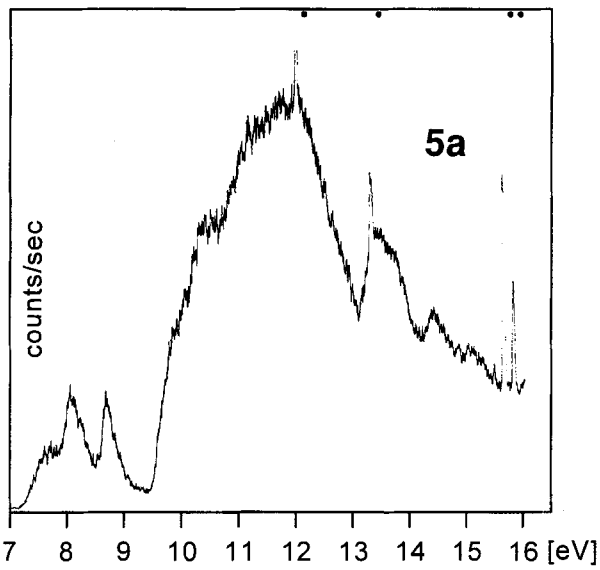
If the distance between the two bridges plays a role, then according to Table 1 a borderline value of 285–290 pm must be responsible for separating the two groups. It is rather unlikely that such a small threshold distance would be mainly responsible for a definite yes/no answer to a [6+2] photo cycloaddition.

More likely the known difference in energy of the azo bridge from DBH and DBO itself may be most important. The different n-π^* transition wavelengths at 360–368 nm for types **1** ($5_C/5_N$) and **3** ($6_C/5_N$) compared to 387–394 nm for types **5** ($5_C/6_N$) and **7** ($6_C/6_N$) present a complex absorption maximum-molecular structure-dependence as has been pointed out by Mirbach et al.[33].

According to Table 3 the n_- ionization energy of the azo bridge is higher by 0.25 eV in **3a** (type **3**, $6_C/5_N$) compared to **5c** and **5a** (type **5**, $5_C/6_N$), and only in the former compound does it match with the π_- ionization of the *o*-phenylene bridge. It is remarkable that this 0.25 eV energy difference of the n_- ionization energies (or orbital energies) between type **3** ($6_C/5_N$, **3a**) and type **5** ($5_C/6_N$, **5a**) corresponds almost exactly to the difference between observed n-π^* transition energies (0.25 eV ≅ 2016 cm^{-1}, which is precisely the energy difference between 400 nm and 370 nm!). It is

Figure 3. He(I) photoelectron spectra of **3a**, **5a** and **5c**; calibration peaks are: Xe (12.130, 13.463 eV) and Ar (15.759, 15.937 eV)





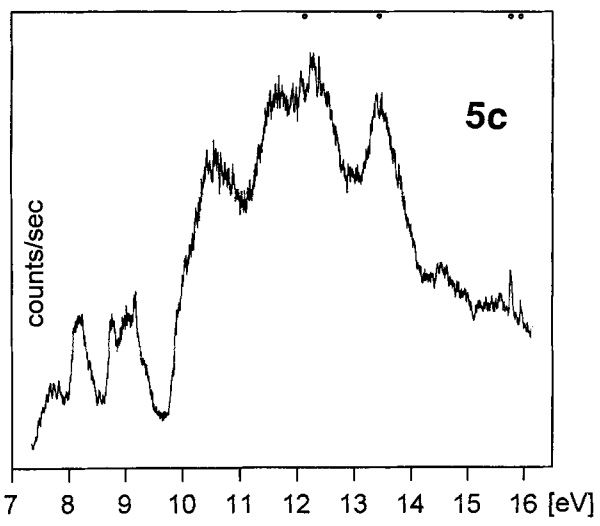


Table 3. Experimental vertical ionization energies I_v [eV] of **3a**, **5a** and **5c** from He(I) photoelectron spectra; accuracy $\Delta I_v \leq 0.05$ eV, in the cases of **3a** and **5a** $\Delta I_v \leq 0.03$ eV; assignment: Semi-empirical MINDO/3 calculations which served also for geometry optimizations[29] (assumption of the validity of Koopmans' theorem); calibration of spectra: Xe (12.130, 13.436 eV), Ar (15.759, 15.937 eV); BO = bicyclooctene olefinic π orbital, Cy = cyclopentene π orbital, B = bicycloheptene olefinic π orbital; in case of **13a** and **5c** a′ and a″ refer to the local symmetry ignoring the cyclopentene double bond (π_{CC}Cy); the PE spectrum of **13a** was thoroughly discussed[30]

Type	Comp.	$I_{v,1}$	$I_{v,2}$	$I_{v,3}$	$I_{v,4}$	$I_{v,5}$
3($6_C/5_N$)	**3a**	8.15	8.15	8.90	9.1 - 9.2	10.2
Assignment		n_-, π_- = (a′(π_{CC})-$\lambda\pi_{NN}$)		a″(π_{CC})	a′(π_{CC}BO)	
5($5_C/6_N$)	**5c**	7.90	8.25	8.85	9.20	>10
	5a	7.90	8.20	8.85	>10	
Assignment		n_-	(a′(π_{CC})-$\lambda\pi_{NN}$)	a″(π_{CC})	π_{CC}Cy	
13($5_C/6_N$) bridge CC	**13a**[4]	7.90	8.65	9.10	>10	
Assignment		n_-	(a′(π_{CC}B)-$\lambda\pi_{NN}$)	π_{CC}Cy		

therefore possible to draw one of the following conclusions: either

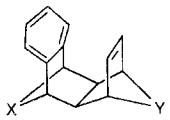
1. the energies of the azo n-π* transitions of **3a** and **5a** are predominantly determined by the n_- ionization energies. In other words the energies of the two azo n-π* configurations of **3a** and **5a** depend predominantly on the n_- orbital energies, or

2. the coincidence of Δn_-(**3a**/**5a**) with $\Delta\nu$(**3a**/**5a**) is more or less fortuitous. In this context it is important to mention that Mirbach et al.[33] did not succeed in establishing a clear-cut correlation between absorption maxima and ionization energies.

But whatever the reason may be for the hypsochromicity of the n-π* transition of type **3** compounds, the following argument can be given. Due to the higher excitation energy of type **3** compounds and due to their higher ground state strain (the ring strain of DBH exceeds that of DBO by about 6 kcal/mol)![33] it has been suggested that a dissociative surface crosses the n-π* state of type **3** (5_N) rather close to the first vibrational level $v' = 0$ but only at higher vibrational levels[34] for type **5** (6_N). It is therefore tempting to assume that the main photochemical differences between systems **1**/**3** and **5**/**7** reflect nothing else than the well-known photochemical difference between DBH and DBO, the latter belonging to the "photochemically reluctant" class of azo compounds[35].

The question of through bond and/or through space 1,5-laticyclic conjugation cannot be answered directly, since the systems with the saturated systems for comparison are missing. However, comparison with the corresponding olefinic bridged systems (Table 2) shows an equal bathochromic shift[15,18] for types **1** and **3** and a somewhat smaller one for types **5** and **1**. Therefore, the extensively discussed 1,5-laticyclic conjugation for the C=C/N=N systems[27] has to be assumed at least for the photoactive types **1** and **3**.

Further information should be gained from the [6+2] photocycloadditions of the four hydrocarbons **48**–**51**, an idea which inspired *Prinzbach* to study **7a**[19].



	48	49	50	51
X	CH_2	$(CH_2)_2$	CH_2	$(CH_2)_2$
Y	CH_2	CH_2	$(CH_2)_2$	$(CH_2)_2$

We are grateful to the *Fonds der Chemischen Industrie* and the *BASF AG*, Ludwigshafen/Rhein, for financial support of this investigation.

Experimental

Physical equipment, solvents etc. cf ref.[1]. Flash chromatography (FLC)[37] on silica gel WOELM, 32–63 μm, 30–45 cm, ∅ 3 cm; medium pressure chromatography (MLPC)[38] on LiChrosorb 15–25 μm (Merck), column 25 × 2.4 cm (theoretical plates N = 7200). UV-detection (254 nm) in both cases. PE spectra were recorded with a UPG 200 Leybold Heraeus spectrometer. The accuracy of I, and the calibration gases are given in Table 3.

Table 4. X-ray data for **1a** and **3a**[39]

compound	**1a**	**3a**
empirical formula	$C_{18}H_{22}N_2$	$C_{17}H_{18}N_2$
molecular mass	266.39	250.35
a [pm]	1528.0(3)	1783.0(5)
b [pm]	1521.8(3)	1200.7(3)
c [pm]	653.0(1)	645.0(2)
β [deg]	91.51(2)	97.70(2)
V [pm³]	1518.5(5)·10⁶	1368.4(7)·10⁶
Z	4	
d(calcd) [g·cm⁻³]	1.165	1.215
crystal system	monoclinic	
space group	$P2_1/n$	
diffractometer	Nicolet R3m/V	
radiation	Mo *Kα*	
monochromator	graphite	
crystal size [mm]	0.4 x 0.75 x 0.25	0.75 x 1.0 x 0.1
data collection mode	*ω*-scan	
theta range [deg]	1.75 → 27.5	
recip. latt. segment	*h* = 0 → 18	*h* = 0 → 21
	k = 0 → 18	*k* = 0 → 14
	l = -7 → 7	*l* = -7 → 7
no. refl. measd.	2884	2728
no. unique refl.	2664	2432
no. refl. $F > 3\sigma(F)$	1900	2029
lin. abs. coeff. [mm⁻¹]	0.06	0.07
abs. correction	*ψ*-scan	
solution by	direct phase determination	
method of refinement	Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic *U*	
data-to-parameter ratio	10.50	11.80
R, R_w	0.053, 0.049	0.050, 0.047
weighting scheme	$w = 1/\sigma^2(F)$	
largest difference peak	0.22 eÅ⁻³	0.22 eÅ⁻³
largest difference hole	0.15 eÅ⁻³	0.17 eÅ⁻³
program used	Siemens SHELXTL PLUS	

Compound **1b**: A solution of **9a** (294 mg, 1.36 mmol)[12] and tetrachlorothiophenedioxid (**21**) in CH_2Cl_2 (4.00 ml) is reacted for 10 d at ambient temperature. The solution is directly chromatographed (CH_2Cl_2). Broad bands indicate oxidation of intermediate **22** on the column. When a yellow zone arrives at the end of the column, elution with MeOH is started. Fraction A): Colourless solid (550 mg) which is redissolved in CH_2Cl_2 (4 ml) and stirred for 3 h in an open vessel to remove traces of **22** (^{1}H-NMR). B): Yellow powder (230 mg) which on further chromatography yields colorless product (118 mg). A) and B) consist of **1b** (468 mg, 85%), mp 223–226°C. – IR (KBr): $\tilde{\nu}$ = 3005 cm^{-1}, 2995, 2980, 2950, 2875 (C–H). – UV (CH_3CN): λ_{max} (log ε) = 372 (2.81), 220 (4.44), 206 (4.46). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.32, 0.88 (2 s, 6H, 11-*exo*-, *endo*-CH_3), 1.60 (s, 6H, 1-, 4-CH_3), 1.77, 1.93 (AB, 2H, 12-H_2, J_{AB} = 9.1 Hz), 2.94–2.95 (m, 2H, 4a-, 10a-H), 3.55–3.57 (m, 2H, 5-, 10-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.34 (q, C-1, -4), 15.94 (q, *exo*-CH_3-11), 17.25 (q, *endo*-CH_3-11), 44.55 (d, C-4a, -10a), 50.15 (d, C-5, -10), 53.72 (t, C-12), 64.20 (s, C-11), 88.52 (s, C-1, -4), 126.77, 130.11 (2 s, C-6, -7, -8, -9), 142.18 (s, C-5a, -9a). – MS (70 eV): *m/z* (%) = 404.1 (0.04 [M$^+$], 365.1 (0.22), 364.1 (0.17), 363.1 (1.04), 362.0 (0.39), 361.1 (2.20), 360.0 (0.33), 359.1 (1.70) [M$^+$ – N_2 – CH_3, Cl isotope], 122.1 (100). – $C_{18}H_{18}Cl_4N_2$ (404.2): calcd. C 53.49, H 4.49, N 6.94; found C 53.44, H 4.60, N 7.06.

Compound **1a**: A solution of **1b** (92.0 mg, 0.23 mmol) in MeOH (5 ml) is hydrogenated with Pd/C (220 mg) and ammonium formiate (120 mg, 1.90 mmol) for 22 h at room temp. After removal of the solvent, the residue is dissolved in (EtOAc/PE, 8:1) and filtered through a pad of silica gel. Yield of **1a**: 50 mg (82%) as colourless solid with mp 109–110°C. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}. – UV (CH_3CN): λ_{max} (lg ε) = 368 nm (2.70), 207 (4.22). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.30, 0.89 (2 s, 6H, 12-*exo*, *endo*-CH_3), 1.55 (s, 6H, 1-, 4-C*H*$_3$), 1.79, 1.96 (AB, 2H, 11-H_2, J_{AB} = 8.5 Hz), 2.91 (m_c, 2H, 4a-, 10a-H), 3.27 (m_c, 2H, 5-, 10-H), 7.09 (m_c, 6-, 7-, 8-, 9-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.51 (q, *C*H_3-1, -4), 15.88 (q, *exo*-CH_3-11), 17.46 (q, *endo*-CH_3-11), 44.27 (d, C-4a, -10a), 51.31 (d, C-5, -10), 55.62 (t, C-12), 64.57 (s, C-11), 88.07 (s, C-1, -4), 121.77, 126.65 (2 d, C-6, -7, -8, -9), 144.12 (s, C-5a, -9a). – MS (70 eV): *m/z* (%) = 266.2 (0.43) [M$^+$], 251.1 (0.14) [M$^+$ – CH_3], 238.1 (0.24) [M$^+$ – N_2], 223.1 (2.35) [M$^+$ – N_2 – CH_3], 116.1 (100). – $C_{18}H_{22}N_2$ (266.4): calcd. C 81.16, H 8.32, N 10.51; found C 80.81, H 8.64, N 10.12.

Compounds **11a** *and* **3a**: At 0°C trifuloroacidic acid (1.20 ml) is added to a solution of the trimeric azine **23** (500 mg, 1.74 mmol)[15] in $CHCl_3$ (4.0 ml). After addition of benzobarrelene (**24**, 802 mg, 5.20 mmol) the mixture is kept for 2 h at 0°C. After 24 h at room temp. another 50 mg (0.17 mmol) of **23** is added since **24** is still present (TLC, EtOAc/PE, 8:1) and the mixture is kept for a further 24 h. After treating with saturated K_2CO_3 solution (10 ml), the phases are separated and the organic layer is extracted with $CHCl_3$ (2 × 15 ml). FLC of the evaporated solution (cyclohexane/EtOAc = 1:1) yields **11a** (249 mg, 30%), mp 147–148°C and **3a** (122 mg, 15%), mp 158–159°C together with reisolated **24** (290 mg, 36%).

Compound **11a**: IR (CCl_4): $\tilde{\nu}$ = 3065 cm^{-1}, 3015 (=C-H), 2975, 2950, 2880 (-C-H), 1625 (C=C), 1495, 1470, 1460 (N=N). 1380, 1360 (C(CH_3)$_2$), 1280, 1240, 1230. – UV (*n*-hexane): λ_{max} (lg ε) = 363 nm (2.57), 353 (2.28), 272 (3.03), 266 (3.03), 258 (2.94). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (s, 3H, 13-*exo*-CH_3), 1.00 (s, 3H, 13-*endo*-CH_3), 2.62 (br. s, 2H, 4a-, 10a-H), 3.80 (mc, 2H, 5-, 10-H), 4.64 (br. s, 1-, 4-H), 5.93 (dd, 2H, 1-, 12-H, *J* = 3 Hz, *J* = 4.5 Hz), 7.06 (AA'BB', 4H, 6-, 7-, 8-, 9-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.04 (q, *exo*-CH_3-13), 19.46 (q, *endo*-CH_3-13), 40.48 (d, C-4a, -10a), 41.84 (d, C-5, -10), 58.91 (s, C-13), 85.83 (d,

C-1, -4), 122.49 (d, C-7, -8), 125.11 (d, C-6, -9), 130.47 (d, C-11, -12), 146.49 (s, C-5a, -9a). – MS (70 eV): *m/z* (%): 207 (3) [M^+ -N_2, -CH_3], 128 (100). – $C_{17}H_{18}N_2$ (250.3): calcd. C 81.56, H 7.25, N 11.19; found C 81.40, H 7.36, N 11.42. – *Compound* **3a**: IR (CCl_4): $\tilde{\nu}$ = 3070, 3050, 3020 (=C–H), 2970, 2950, 2930, 2875 (–C–H), 1600 (C=C), 1490, 1475, 1450 (N=N), 1395, 1380 [$C(CH_3)_2$], 1340, 1330, 1280, 1230. – UV (*n*-hexane): λ_{max} (lg ε) = 364 (2.81), 353 (2.43), 270 (sh, 2.87), 256 (sh, 2.94), 250 (sh, 2.96). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.55 (s, 3H, 13-*exo*-CH_3), 1.09 (s, 3H, 13-*endo*-CH_3), 2.84 (br. s, 2H, 4a-, 10a-H), 3.82 (mc, 2H, 5-, 10-H), 4.45 (br. s, 2H, 1-, 4-H), 6.65 (dd, 2H, 11-, 12-H), 7.08 (AA'BB', 4H, 6-, 7-, 8-, 9-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.21 (q, *exo*-CH_3-13), 19.55 (q, *endo*-CH_3-13), 41.38 (d, C-4a, -10a), 44.10 (d, C-5, -10), 59.81 (s, C-13), 85.52 (d, C-1, -4), 123.41 (d, C-7, -8), 126.23 (d, C-6, -9), 138.76 (d, C-11, -12), 141.40 (s, C-5a, -9a). – MS (70 eV): *m/z* (%): 250 (2) [M^+], 235 (11) [M^+ – CH_3], 207 (4) [M^+CH_3, -N_2], 192 (6) [M^+-N_2, -2CH_3], 128 (100). – $C_{17}H_{18}N_2$ (250.3); calcd. C 81.52, H 7.25, N 11.18; found: C 81.31, H 7.40, N 1142.

Compound **3b**: Catalytic hydrogenation of **3a** (100 mg, 0.40 mmol) in EtOAc (7.0 ml) with Pd/C (120 mg) for 2.5 h and MLPC of the product (EtOAc/PE, 1:1) yields **3b** (70 mg, 69%) with mp 140–142°C after sublimation. Longer hydrogenation times produce mainly decomposition products. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3025 (=C-H). -UV (CH_3CN): λ_{max} (lg ε) = 360 (2.67), 350 (2.39). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.53, 1.09 (2 s, 6H, 11-*exo*, -*endo*-CH_3), 1.27–1.40 (m, 2H), 1.64–1.76 (m, 2H), 12-, 13-H_2), 2.69 (m_c, 2H, 1a-, 4a-H), 3.10 (s, 2H, 5-, 10-H), 4.59 (s, 2H, 1-, 4-H), 6.97–7.03 (m, 2H), 7.15–7.22 (m, 2H), (6-, 7-, 8-, 9-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.69, 19.09 (2 q, CH_3-*endo*-, *exo*-11), 27.45 (t, C-12, -13), 35.43 (d), 41.34 (d), 56.62 (s, C-11), 87.09 (d, C-1, -4), 123.71 (d, C-7, -8), 126.67 (C-6, -9), 139.91 (s, C-5a, -9a). – MS (70 eV): *m/z* (%) = 252.1 (0.65, M^+), 224.2 (0.59, M^+ – N_2), 130.0 (100). – $C_{17}H_{20}N_2$ (252.4): calcd. C 80.91, H 7.99, N 11.10; found C 80.54, H 8.21, N 11.35.

Compound **3c**: A mixture of **11a** (250 mg, 1.00 mmol) and **21** (260 mg, 1.02 mmol) in benzene (3 ml) is heated at reflux for 42 h. After removal of the solvent and FLC (ETOAc/PE, 1:8) 280 mg (64%) of **3c** is isolated as a colourless solid with mp 267–268°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3040 (=C-H). – UV (CH_3CN): λ_{max} (lg ε) = 367 (2.81), 298 (2.66), 288 (2.74), 225 (4.50). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.61, 1.02 (2 s, 6H, 17-*exo*-, *endo*-CH_3), 2.91 (br. s, 2H, 4a-, 10a-H), 4.73, 4.81 (2 s, 4H, 1-, 4-, 5-, 10-H), 7.12–7.14 (m, 2H), 7.28–7.30 (m, 2H), (12-, 13-, 14-, 15-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.91, 19.25 (2 q, CH_3-*endo*-, *exo*-17), 42.54 (d), 43.03 (d), 59.26 (s, C-17), 85.73 (d, C-1, -4), 123.95 (d), 126.74 (d), 128.11 (s), 130.35 (s), 138.72 (s), 143.18 (s). – MS (70 eV): *m/z* (%) = 439.8 (0.04), 437.9 (0.11), 435.8 (0.07) [M^+, Cl isotope], 409.6 (0.04), 407.8 (0.03) [M^+ – N_2, Cl isotope], 315.8 (100). – $C_{21}H_{16}Cl_4N_2$ (438.2): calcd. C 57.75, H 3.68, N 6.39; found C 57.81, H 3.58, N 6.46.

Compound **3d**: In a mixture of MeOH (3.0 ml) and benzene (3.0 ml) **3c** (120 mg, 0.27 mmol) reacts with ammonium formiate (140 mg, 2.22 mmol) and Pd/C (210 mg) for 3.5 d at room temp. The crude product is purified by MPLC (PE/EtOAc, 2:1) and affords 25 mg (31%) of **3d** as a colourless solid, mp 223°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3050, 3030. – UV (CH_3CN): λ_{max} (lg ε) = 362 (2.70), 352 (2.40), 272 (3.00), 263 (3.06), 256 (3.06). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.58, 1.01 (2 s, 6H, 17-*exo*-, *endo*-CH_3), 2.89 (br. s, 2H, 4a-, 10a-H), 4.25 (s, 2H, 5-, 10-H), 4.65 (s, 2H, 1-, 4-H), 7.06 (m_c, 2H), 7.13 (s, 4H), 7.23 (m_c, 2H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.19, 19.40 (2 q, CH_3-*exo*-, *endo*-17), 44.27 (d), 45.76 (d), 59.35 (s, C-17), 86.21 (d, C-1, -4), 123.32 (d), 124.01 (d), 125.80 (d), 126.80 (d), 140.54 (s), 145.67 (s). – MS (70 eV): *m/z* (%) = 300.0 (0.25) [M^+], 272.0 (0.19) [M^+ – N_2], 178.0 (100). – $C_{21}H_{20}N_2$ (300.4): calcd. C 83.96, H 6.72, N 9.32; found C 83.65, H 6.84, N 8.99.

Compound **25**: A mixture of **13** (1.01 g, 3.96 mmol)[12] and **21** (841 mg, 3.96 mmol) in $CHCl_3$) (or CH_2Cl_2, toluene, 10 ml) reacts within 7 d/TLC. After evaporation of the solvent FLC yields **25** (1.40 g, 88%), mp 166–168°C, together with some **5b** (2.6%). – IR ($CDCl_3$): $\tilde{\nu}$ = 3030 cm^{-1} (=C–H), 2980–2850 (–C–H). – UV (*n*-hexane): λ_{max} (lg ε) = 387 (2.44), 377 (2.12). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.33 (*A*B, 1H, 12-H), 1.72 (A*B*, 1H, 12′-H), 2.32 (mc, 2H, 4a-, 10a-H), 2.42 (m, 4H, 3-, 3′-, 5a-, 9a-H), 2.68 (m, 3H, 5-, 10-, 11a-H), 3.03 (m, 1H, 11a-H), 5.46 (mc, 2H, 4-, 11-H), 5.60 (s, 2H, 1-, 2-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 37.38 (t), 38.32 (t), 39.92 (d), 46.49 (d), 46.56 (d), 48.11 (d), 48.17 (d), 48.17 (d), 49.19 (d), 49.27 (d), 51.90 (d), 67.54 (d), 123.35 (s), 129.45 (d), 131.20 (s), 132.66 (d). – MS (70 eV): *m/z* (%) = 402.1 (15.1) [M^+], 81.1 (100). – $C_{18}H_{16}N_2$ (402.2): calcd. C 53.76, H 4.01, N 6.97; found C 54.11, H 4.15, N 7.08.

Compound **5b**: For dehydrogenation **25** (400 mg, 0.99 mmol) is heated at reflux in toluene (20 ml, 29 h) in the presence of air. The residue from the evaporated solution is dissolved in CH_2Cl_2/EtOAc = 10:1 and filtered through a short column of silica gel. Yield of **5b**: 367 mg (93%), mp 274–276°C. – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (=C–H), 2980–2840 (-C–H), 1460, 1440 (N=N), 1380, 1375, 1360, 1290, 1280, 1230, 1160, 1150, 1130, 1110. – UV (*n*-hexane): λ_{max} (lg ε) = 388 (2.40). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.60 (*A*B, 1H, 12-H), 1.80 (A*B*, 1H, 12′-H), J_{AB} = 9.0 Hz), 2.03–2.63 (m, 3H, 3-, 3′-, 3a-H), 2.75 (br. s, 2H, 4a-, 10a-H), 2.82–3.27 (m, 1H, 3a-H), 3.63 (mc, 2H, 5-, 10-H), 5.28 (br. s, 2H, 4-, 11-H), 5.40 (br. s, 2H, 1-, 2-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 36.99 (t), 39.47 (d), 43.41 (d), 47.25 (d), 49.71 (t), 51.47 (d), 66.33 (d), 68.27 (d), 129.17 (d), 139.54 (d), 142.42. – MS (70 eV): *m/z* (%) = 400.6 (0.3) [M^+], 118.3 (100). – $C_{18}H_{14}N_2$ (400.2): calcd. C 54.03, H 3.53, N 7.00; found C 54.22, H 3.32, N 6.95.

Compound **5a**: A suspension of **5b** (238 mg, 0.59 mmol), ammonium formiate (403 mg, 7.9 mmol) and Pd/C (230 mg) in methanol (5 ml) is stirred for 48 h. After evaporation of the solvent and filtration of the dissolved residue (CH_2Cl_2/EtOAc, 20:1) through a pad of silica gel a colourles solid of **5a** (133 mg, 85%), mp 165°C, is isolated. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3030, 3005. – UV (CH_3CN): λ_{max} (lg ε) = 391 (2.27), 276 (2.55), 269 (2.67), 206 (4.20). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04–1.11 (m, 1H), 1.16–1.26 (m, 3H), 1.58–1.66 (m, 3H), 1.80 (AB, 1H, 14-H, J_{AB} = 8.7 Hz), 2.24 (m_c, 2H), 2.61 (m_c, 2H), 3.26 (pt, 2H, 5-, 10-H), 5.14 (s, 2H, 4-, 11-H), 7.09–7.14 (m, 4H, 6-, 7-, 8-, 9-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.13 (t, C-2), 30.08 (t, C-1, -3), 44.81 (d), 44.90 (d), 46.89 (d), 51.82 (t, C-12), 68.26 (d, C-4, -11), 121.77 (d), 127.00 (d), 144.36 (s, C-5a, -9a). – MS (70 eV): *m/z* (%) = 264.2 (0.91) [M^+], 236.1 (4.52) [M^+ – N_2], 116.0 (100). – $C_{18}H_{20}N_2$ (264.4): calcd. C 81.78, H 7.62, N 10.60; found C 82.14, H 7.17, N 10.55.

Anhydride **26**[17]: Insoluble polymers can be avoided if the reported procedure[17] is changed: A solution of maleic anhydride (15.0 g, 0.15 mol), indene (25.0 g, 0.21 mol) and phenothiazine (0.50 g) as a radical quencher in benzene (25 ml) is heated in an autoclave (glass insert) for 5 h to 250°C. From the cooled solution the crystals are separated and washed with cold EtOAc. The crude product was recrystallized (13.8 g, 37%), mp 187–188°C

(187–188 °C[17]). Without phenazine only 5% of **26** could be isolated.

Diol **27**: To a suspension of $LiAlH_4$ (11.2 g, 295 mmol) in THF (500 ml) at 5 °C **26** (31.7 g, 148 mmol) is slowly added under N_2, whereby the temperature may raise to ca. 27 °C. Heating at reflux for 3 h and cooling to 0 °C, successive addition of [H_2O 11.2 ml, 15 perc. NaOH (11.2 ml)] and H_2O (34.0 ml) produces an easily removable precipitate. *Diol* **27** is isolated from the solution (21.5 g) and by extraction of the precipitate (CH_2Cl_2, 36 h, 8.40 g). Overall yield of **27**: 29.9 g (99%), mp 102–104 °C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH). – ^1H NMR (60 MHz): δ = 1.79 (AB, 2H), 2.54–2.89 (m, 4H), 3.25 (s, 2H, 3.41 (d, 2H), 4.19 (br. s, 2H, OH), 7.10 (m_c, 4H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 43.42 (d), 47.44 (d), 49.82 (t, C-9), 62.77 (t, CH_2OH), 122.16 (d), 125.52 (d), 144.46 (s).

Compounds **5c** *and* **31** via **27** → **28** → **29**: To oxalyl chloride (11.0 ml, 121 mmol) in CH_2Cl_2 (100 ml) at −60 °C is added DMSO (18.7 ml, 242 mmol) in CH_2Cl_2 (30 ml). After 5 min a solution of **27** (10.2 g, 55.0 mmol) in CH_2Cl_2/DMSO (100: 5.0 ml) is slowly added at −50 °C. After 2 h and addition of NEt_3 (75.0 ml) the mixture is warmed to room temp. and extracted with 2 N HCl, sat. $NaHCO_3$ and sat. NaCl solution. On evaporation of the dried (K_2CO_3) solution (103 g), a yellow solid remains (crude **28**). A mixture of **28** (9.30 g) in CH_2Cl_2 (80.0 ml), K_2CO_3 (13.5 g) and hydrazine hydrate (100%, 5.0 ml) is stirred for 4.5 d at room temp. From the filtered and evaporated solution crude **29** (9.00 g) is isolated. To a solution of crude **29** (3.00 g) in CH_2Cl_2 (15.0 ml) at 0 °C are added cyclopentadiene (**30**, 10.0 ml), after 1 d another 5.0 ml one day later, and finally trifluoro acetic acid (1.50 ml, 19.8 mmol). After 3 d at 6–8 °C the solution is extracted with sat. $NaHCO_3$ and dried (K_2CO_3). Removal of the solvent and FLC of the residue (CH_2Cl_2/EtOAc, 1:1) yields a colourless powder of **31** (237 mg, 5%), mp 257–259 °C and a brownish solid of **5c** (1.66 g). Sublimation affords colourless **5c** (1.51 g, 35%), mp 197–199 °C. – *Compound* **5c**: IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3020 (=C–H), 2980–2840 (–C–H), 1470, 1460, 1450 (N=N), 1350, 1315, 1270, 1150, 1120, 1010. – UV (*n*-hexane): λ_{max} (lg ε) = 387 (2.27). – ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.65 (*A*B, 1H, 12-H), 1.82 (A*B*, 1H, 12′-H, J_{AB} = 8.8 Hz), 2.14 (*A*B, 1H, 3-H), 2.35 (A*B*, 1H, 3′-H, J_{AB} = 17.5 Hz), 2.52 (m, 1H, 3a-H), 2.68 (dd, 2H, 4a-, 10a-H), 2.96 (m, 1H, 11a-H), 3.26 (br. s, 2H, 5-, 10-H), 5.14 (s, 1H), 5.18 (s, 1H) (1-, 2-H), 5.48 (m, 2H, 4-, 11-H), 7.10 (m, 4H, 6-, 7-, 8-, 9-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 36.96 (t), 40.09 (d), 44.67 (d), 44.76 (d), 47.14 (d), 51.61 (t), 52.13 (d), 66.79 (d), 68.74 (d), 121.93 (d), 122.01 (d), 127.17 (d), 127.22 (d), 129.50 (d), 132.17 (d), 144.31. – MS (70 eV): *m/z* (%) = 262 (1.4) [M^+], 116.1 (100). – $C_{18}H_{18}N_2$ (262.4): calcd. C 82.41, H 6.92, N 10.68; found C 82.51, H 6.98, N 10.33. – *Compound* **31**: IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 3005. – UV (CH_3CN): λ_{max} (lg ε) = 393 (1.69), 378 (1.59), 354 (1.22), 272 (2.91), 265 (2.93); 258 (2.80). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.38, 1.74 (AB, 2H, 12-H_2, J_{AB} = 10.3 Hz), 1.94 (m_c, 2H), 2.26–2.51 (m, 3H), 2.91–2.96 (m, 1H, 3a-H), 3.32, 3.33 (2 s, 2H, 5-, 10-H), 5.53 (m_c, 2H, 2-, 3-H), 5.66, 5.70 (2 s, 2H, 4-, 11-H), 7.06 (m_c, 4H, 6-, 7-, 8-, 9-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 37.15 (t), 38.96 (d), 44.22 (t), 44.88 (d), 44.97 (d), 47.88 (d, 2 C), 51.01 (d), 69.25, 71.36 (2 d, C-, -11), 120.04 (d), 120.13 (d), 125.68 (d, 2 C), 129.57 (d), 132.54 (d), 149.09 (s), 149.22 (s). – $C_{18}H_{18}N_2$ (262.4): calcd. C 82.41, H 6.91, N 10.68; found C 82.12, H 6.91, N 10.74.

Compounds **5d** and **33**: According to the procedure for **5c** and **31**, diol **27** (2.00 ml, 22.0 mmol) is transformed into **28** (oxalyl chloride, 2.00 ml, 22.0 mmol; DMSO, NEt_3, 15.0 ml, 107 mmol) and then into the trimeric triazine **29** (K_2CO_3, 3.0 g), hydrazine hydrate (1.00 ml). A solution of crude **29** (0.94 g) and norbornene (**32**) (4.00 g, 42.5 mmol) and trifluoroacetic acid (0.50 ml, 6.60 mmol) in CH_2Cl_2 (15.0 ml) is reacted for 1 d at 6–8 °C and 18 h at room temp. The crude product (see **5c/31**) is chromatographed (CH_2Cl_2/MTB, 10:1, detect. 375 nm): **33** (12 mg, 1%), mp 242–244 °C and **5d** [418 mg, yellowish powder, from cyclohexane (365 mg, 27%) colourless crystals], mp 179–181 °C. – *Compound* **5d**: IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 3025. – UV (CH_3CN): λ_{max} (lg ε) = 390 (2.33), 276 (2.55), 268 (2.68). – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.49, 1.08 (AB, 2H, 13-H_2, *J* = 10.7 Hz), 0.99 (m_c, 2H), 1.34 (m_c, 2H), 1.73 (s, 2H), 1.59, 1.76 (AB, 2H, 14-H_2, *J* = 8.7 Hz), 2.08 (br. s, 2H), 2.61 (br. s, 2H), 3.26 (t, 2H, 6-, 11-H, *J* = 1.7 Hz), 5.17 (s, 2H, 5-, 12-H), 7.11 (m_c; 7-, 8-, 9-, 10-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.85 (t, C-, -3), 34.78 (t, C-13), 40.05 (d), 45.27 (d), 46.79 (d), 48.52 (d), 51.28 (t, C-14), 68.05 (d, C-5, -12), 121.56, 126.85 (2 d, C-7, -8, -9, -10), 144.09 (s, C-6a, -10a). – MS (70 eV): *m/z* (%) = 290.1 (0.75) [M^+], 262.1 (3.89) [$M^+ - N_2$], 116.1 (100). – $C_{20}H_{22}N_2$ (290.1): calcd. C 82.72, H 7.63, N 9.64, found C 83.01, H 7.89, N 9.69. – *Compound* **33**: IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1}, 3020. – UV (CH_3CN): λ_{max} (lg ε) = 393 (1.64), 3.77 (1.56), 353 (1.20), 271 (2.85), 265 (2.88), 259 (2.74). – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.65 (A*B*), 1H, 13-H′, *J* = 10.7 Hz), 0.96 (m_c, 2H), 1.20–1.26 (m, 2H), 1.38 (m_c = 2H), 1.67 (*A*B, 1H, 14-H, J_{AB} = 10.4 Hz), 1.69 (s, 2H), 1.87 (s, 2H), 2.22 (br. s, 2H), 3.29 (t, 2H, 6-, 11-H, *J* = 1.3 Hz), 5.66 (s, 2H, 5-, 12-H), 7.05 (m_c; 4-H, 7-, 8-, 9-, 10-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.05 (t, C-2, -3), 35.09 (t, C-13), 40.54 (d), 44.30 (t, C-14), 46.06 (d), 47.82 (d), 48.06 (d), 70.90 (d), C-5, -12), 120.07, 125.74 (2 d, C-7, -8, -9, -10), 149.74 (s, C-6a, -10a). – MS (70 eV): *m/z* (%) = 290.3 (0.94 [$M^+ - N_2$], 262.1 [$M^+ - N_2$], 116.1 (100). – $C_{20}H_{22}N_2$ (290.4): C 82.72, H 7.63, N 9.64, found C 82.51, H 7.59, N 9.30.

Compounds **5e** *and* **35**: In analogy to **5d** and **33** crude **29** (1.00 g) reacts with norbornadiene (**34**, 5.0 ml). The first fraction from FLC (23 mg) yields **35** (14 mg, 1%) after MPLC (PE/ETOAc, 15:1, detect. 380 nm) as a colourless solid, mp 265–267 °C. The second fraction (363 mg) affords **5e** (325 mg, 22%) as a colourless solid, mp 141–144 °C after filtration through a pad of silica gel (PE/EtOAc, 4:1). – *Compound* **5e**: IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 3030. – UV (CH_3CN): λ_{max} (lg ε) = 393 (2.26). – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78, 1.26 (AB, 2H, 13-H_2, J_{AB} = 9.7 Hz), 1.78 (s, 2H), 1.65, 1.81 (AB, 2H, 1.65, 1.81 (AB, 2H, 14-H_2, J_{AB} = 8.8 Hz, J'_A = 1.7 Hz, J'_B = 1.4 Hz), 2.66–2.68 (m, 4H), 3.27 (t, 2H, 6-, 11-H, *J* = 1.7 Hz), 5.17 (s, 2H, 5-, 12-H), 6.05 (t, 2H, 2-, 3-H, *J* = 1.6 Hz), 7.12 (m_c, 4H, 7-, 8-, 9-, 10-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 42.75 (t, C-13), 45.16 (d), 45.49 (d), 45.79 (d), 46.64 (d), 51.77 (t, C-14), 67.02 (d, C-5, -12), 121.52, 126.83 (2 d, C-7, -8, -9, -10), 138.76 (d, C-2, -3), 144.06 (s, C-6a, -10a). – MS (70 eV): *m/z* (%) = 288.2 (1.81) [M^+], 260.1 (1.67 [$M^+ - N_2$], 116.1. – $C_{20}H_{20}N_2$ (288.4): C 83.30, H 6.99, N 9.71, found C 83.58, H 7.01, N 9.47. – *Compound* **35**: IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3020 (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 396 (1.50), 381 (1.50), 356 (1.27), 321 (1.70), 272 (2.97), 264 (3.15), 248 (3.25). – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94, 1.39 (AB, 2H, 13-H_2, *J* = 9.6 Hz), 1.27, 1.71 (AB, 2H, 14-H_2, *J* = 10.3 Hz), 1.73 (s, 2H), 1.91 (s, 2H), 2.80 (q, 2H, 1-, 4-H, *J* = 1.6 Hz, 3.31 (t, 2H, 6-, 11-H, *J* = 1.4 Hz), 5.64 (s, 2H, 5-, 12-H), 6.05 (t, 2H, 2-, 3-H, *J* = 1.6 Hz), 7.04 (m_c, 4H, 7-, 8-, 9-, 10-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.13 (t), 44.42 (t), 44.91 (d), 45.76 (d), 46.82 (d), 48.00 (d), 70.11 (d, C-5, -12), 120.12, 125.80 (C-8, -9, -10), 138.99 (d, C-2, -3), 149.52 (s, C-6a, -10a). – MS (70 eV): *m/z* (%) = 288.1 (0.90) [M^+], 260.1 (0.89) [$M^+ - N_2$], 116.1 (100). – $C_{20}H_{20}N_2$ (288.4): calcd. C 83.30, H 6.99, N 9.71, found C 83.18, H 6.85, N 9.40.

Compounds **5f** *and* **15a**: Crude **29** (1.02 g, see **5d/33**) and benzobarrelene (**24** 800 mg, 5.20 mmol) are heated at reflux with trifluoroacetic acid (1.20 ml, 15.6 mmol) in benzene (10 ml) for 43 h. After addition of EtOAc (30 ml) the mixture is extracted with sat. $NaHCO_3$ solution and dried (K_2CO_3). FLC (EtOAc/PE, 1:1) yields **24** (196 mg, 25%) together with **15a** (107 mg) and **5f** (697 mg) as brownish solids. After MPLC (EtOAc/PE, 1:1) pure **5f** (87 mg, 5%) is isolated as a colourless solid, mp 243–246°C. Crude **15a** yields colourless **15a** (430 mg, 24%), mp 239–246°C (turns dark > 200°C) from CH_2Cl_2/EtOAc. – *Compound* **5f**: IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3050, 3020. – UV (CH_3CN): λ_{max} (lg ε) = 394 (2.38). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.59, 1.78 (AB, 2H, 17-H_2, J_{AB} = 8.8 Hz), 2.13 (br. s, 2H), 2.61 (br. s, 2H), 3.26 (s, 2H, 7-, 12-H), 3.78 (t, 2H, 5-, 14-H, J = 3.8 Hz), 5.10 (s, 2H, 6-, 13-H), 5.91 (m_c, 2H, 15-, 16-H), 7.02–7.25 (m, 8H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 42.40 (d), 44.05 (d), 46.35 (d), 46.79 (d), 52.05 (t, C-17), 67.20 (d, C-6, -13), 121.54 (d), 122.27 (d), 125.16 (d), 127.13 (d), 131.59 (d, C-15, -16), 144.07 (s), 144.92 (s). – MS (70 eV): *m/z* (%) = 350.0 (1.70 [M^+], 322.1 (1.20) [$M^+ - N_2$], 116.0 (100). – $C_{25}H_{22}N_2$ (350.5): calcd. C 85.68, H 6.33, N 7.99, found C 85.44, H 6.30, N 8.02. – *Compound* **15a**: IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3020 (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 398 (1.68), 383 (1.59), 358 (1.15), 272 (3.02), 265 (3.11), 258 (3.05). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.23, 1.66 (AB, 2H, 17-H_2, J_{AB} = 10.3 Hz), 1.86 (s, 2H), 2.07 (s, 2H), 3.28 (br. s, 2H, 7-, 12-H), 3.85 (t, 2H, 5-, 14-H, J = 3.7 Hz), 5.53 (s, 2H, 6-, 13-H), 6.02–6.06 (m, 2H, 15-, 16-H); 6.96–7.10 (m, 8H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 41.20 (d), 44.19 (d), 44.40 (t, C-17), 46.83 (d), 47.81 (d), 69.80 (d, C-5, -14), 120.02 (d), 122.33 (d), 125.30 (d), 125.73 (d), 131.93 (d, C-15, -16), 144.64 (s), 149.16 (s). – MS (70 eV): *m/z* (%) = 350.1 (2.90) [M^+], 322.1 (1.84) [$M^+ - N_2$], 116.0 (100). $C_{25}H_{22}N_2$ (350.5): calcd. C 85.68, H 6.33, N 7.99; found C 85.52, H 6.34, N 8.01. – *Compound* **5g**: Catalytic hydrogenation of **5f** (150 mg, 0.43 mmol) with Pd/C (100 mg) in EtAOc (15 ml) for 22 h at room temp. affords **5g** (149 mg, 98%), mp 269–270°C after filtration through a pad of silica gel (EtOAc/PE, 1:1).

Compound **5g**: Catalytic hydrogenation of **5f** (150 mg, 0.43 mmol) with Pd/C (100 mg) in EtOAc (15 ml) for 22 h at room temp. yields **5g** (149 mg, 98%), mp 269–270°C after filtration through a pad of silica gel (ETOAc/PE, 1:1). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3030 (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 380 (2.50), 268 (3.01), 261 (3.06), 253 (3.04). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.96–1.19 (m, 4H, 15-, 16-H_2), 1.63, 1.82 (AB, 2H, 17-H_2, J_{AB} = 8.7 Hz), 1.93 (s, 2H), 2.63 (s, 2H), 2.84 (s, 2H, 5-, 14-H), 3.32 (s, 7-, 12-H), 5.14 (s, 2H, 6-, 13-H), 7.09–7.26 (m, 8H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.09 (t, C-15, -16), 37.64 (d), 45.89 (d), 46.19 (d), 47.07 (d), 52.37 (t, C-17), 68.51 (d, C-6, -13), 121.75 (d), 123.43 (d), 125.91 (d), 127.03 (d), 144.26 (s), 144.68 (s). – MS (70 eV): *m/z* (%) = 352.1 (0.81) [M^+], 324.1 (0.73), [$M^+ - N_2$], 115.9 (100). – $C_{25}H_{24}N_2$ (352.5): calcd. C 85.19, H 6.89, N 7.95; found C 84.91, H 6.93, N 7.83.

Compound **44**: Compound **42** (100 mg, 0.40 mmol) and tetrachlorothiophenedioxide (**21**: 100 mg, 0.40 mmol) in benzene (3.0 ml) and dichloromethane (1.0 ml) were stirred at room temp. for 13 d. Then excess **21** (50 mg, 0.20 mmol) was added and the mixture stirred for another 12 d. After removal of the solvent, the product was dissolved (residue 25 mg) in dichloromethane and filtered through a pad of silica gel (CH_2Cl_2/ETOAc, 50:1). From the filtrate **44** (118 mg, 67%) was isolated as a colourless solid, mp 141°C, dec. together with **45** (8%, *vide infra*). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}. – UV (CH_3CN): λ_{max} (lg ε) = 387 (2.48), 377 (2.34), 3.49 (1.67), 312 (3.52), 299 (3.74), 286 (3.71), 276 (3.59). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.14–1.18 (m, 2H), 1.42–1.46 (2-, 3-H_2), 1.27, 1.66 (AB, 2H, 15-H_2, J_{AB} = 10.5 Hz), 2.04 (s, 2H), 2.30–2.31 (m, 2H), 2.39 (d, 2H, J = 1.2 Hz), 2.56 (br. s, 2H), 2.62–2.64 (m, 2H), 5.18 (s, 2H, 5-, 12-H), 5.81 (m_c, 2H, 13-, 14-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.53 (t, C-2, -3), 33.68 (d), 37.94 (t, C-15), 41.62 (d), 48.15 (d), 48.43 (d), 49.31 (d), 68.74 (d, C-5, -12), 123.20 (s), 130.87 (d, C-13, -14), 131.26 (s). – MS (70 eV): *m/z* (%) = 448.0 (0.06), 447.1 (0.23), 446.1 (1.14), 445.1 (1.27), 444.0 (5.33), 443.0 (2.89), 442.0 (10.63), 441.0 (2.63), 440.1 (8.23), 439.1 (0.48 [M^+, Cl isotope], 81.0 (100). – $C_{21}H_{20}Cl_4N_2$ (442.2): calcd. C 57.04, H 4.56, N 6.33; found C 56.76, H 4.35, N 6.30.

Compound **43**: In the presence of air **44** (26.0 mg, 0.06 mmol) in toluene (2.0 ml) was heated under reflux for 5 h. After MPC (silica gel, CH_2Cl_2/ETOAc, 50:1) product **43** (20 mg, 76%) was isolated as a colourless solid, dec. >210°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 398 (2.34), 211 (4.48). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07–1.11 (m, 2H), 1.38–1.42 (m 2H), 2-, 3-H_2), 1.57, 1.71 (AB, 2H, 15-H_2, J_{AB} = 9.2 Hz), 2.02 (s, 2H), 2.46 (br. s, 2H), 2.72 (m_c, 2H), 3.58 (m_c, 2H, 5-, 12-h), 5.67 (m_c, 2H, 13-, 14-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.62 (t, C-2, -3), 33.47 (d), 41.69 (d), 45.00 (d), 47.24 (d), 50.21 (t, C-15), 67.47 (d, C-5, -12), 126.71 (s), 130.57 (s), 130.65 (d, C-13, -14), 142.30 (s). – MS (70 eV): *m/z* (%) = 446.0 (0.37), 444.9 (0.96), 443.9 (4.53), 443.0 (4.79), 442.0 (20.39), 441.0 (10.21), 440.1 (41.18), 438.9 (9.02), 438.0 (31.69), 437.1 (1.09), 436.0 (0.47) [M^+, Cl isotopes], 413.9 (0.40), 413.1 (0.37), 412.1 (0.89), 411.1 (0.29), 409.9 (0.72) [$M^+ - N_2$], 158.0 (100). – $C_{21}H_{18}Cl_4N_2$ (440.19): calcd. C 57.30, H 4.12, N6.36; found C 57.05, H 4.18, N 6.42.

Compound **5h**: Under N_2 **44** (80.0 mg, 0.18 mmol) in toluene (5.0 ml) was heated to reflux for 9 h. The solution was filtered through a short column of silica gel and eluted with CH_2Cl_2/ETOAc, 50:1, later 20:1. Fraction 1 (42 mg), purified by MLC (CH_2Cl_2/ETOAc, 50:1), yielded **5h** (38 mg, 50%), mp 263–264°C and **43** (2 mg, TLC). – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1}, 2950, 2910, 2870. – UV (CH_3CN): λ_{max} (lg ε) = 387 (2.58), 218 (4.50), 206 (4.49). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85 (d, 2H, J = 8.7 Hz), 1.10 (d, 2H, J = 8.7 Hz), 1.43 (s, 4H), 1.49 (s, 2H), 1.61, 1.75 (AB, 2H, 15-H_2, J = 9.2 Hz), 1.92 (s, 2H), 2.75 (m_c, 2H), 3.62 (m_c, 2H, 6-, 11-H), 5.08 (s, 2H, 5-, 12-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 23.16 (t, C-13, -14, t, C-2, -3), 27.50 (d), 44.88 (d), 45.31 (d), 47.48 (d), 50.36 (t, C-15), 68.29 (d, C-5, -12), 126.87 (s), 130.39 (s), 142.51 (s). – MS (70 eV): *m/z* (%) = 446.1 (0.07), 445.1 (0.10), 444.2 (0.37), 443.2 (0.24), 442.2 (0.79), 441.2 (0.19), 440.2 (0.61) [M^+, Cl isotope], 416.1 (0.16), 415.2 (0.07), 414.1 (0.37), 413.1 (0.07), 412.1 (0.31 [M^+-N_2], 160.4 (100). – $C_{21}H_{20}Cl_4N_2$ (442.2): calcd. C 57.04, H 4.56, N 6.33; found C 57.16, H 4.62, N 6.20.

Irradiation Experiments: A solution (0.5–1 ml) of the compound placed in an NMR tube (Pyrex) was irradiated with a mercury lamp (high pressure, Heraeus Hanau, TQ-150, 150 W). The tube was fixed in a large tube which contained the lamp and immersed into a methanol cooling bath. The photoreaction was monitored by TLC.

Compound **2a** *(X = H):* A) Compound **1a** (X = H, 20.0 mg, 0.07 mmol) in $CDCl_3$ (0.6 ml), 1 h irradiation at 50°C. – MPC (CH_2Cl_2/EtOAc, 10:1) yielded **2a** (X = H), 16 mg, 80%) as a colourless powder, mp 89–90°C. – B) Compound **1a** (X = H, 30.0 mg, 0.11 mmol) in CH_2Cl_2 (0.9 ml), irradiation for 1 h at 8°C. After removal of the solvent the residue was sublimed (90°C, 0.01 Torr), yielding **2a** (X = H), 27 mg, 90%), mp 89–91°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3040 (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 271 (3.43), 264 (3.43). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91, 0.93 (2 s, 6H, 16-*endo*-, *exo*-CH_3), 1.03 (s, 6H, 1-, 10-CH_3),

1.80, 1.97 (AB, 2H, 13-H_2), 2.55 (m_c, 2H, 12-, 14-H), 2.70 (pt, 2H, 11-, 15-H), 5.68, 5.90 (2 m_c, 4-, 5-, 6-, 7-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.09 (q, CH_3-1, -10), 18.06, 21.10 (2 q, CH_3-*exo*-, *endo*-16), 36.64 (t, C-13), 52.09 (d), 54.08 (s, C-16), 58.18 (d), 73.77, 78.95 (2 s, C-3, -8, -1, -10), 125.06, 125.84 (2 d, C-4, -5, -6, -7). – MS (70 eV): *m/z* (%) = 266.3 [M^+], 116.1 (100). – $C_{18}H_{22}N_2$ (266.4): calcd. C 81.16, H 8.32, N 10.51; found C 80.76, H 8.28, N 10.16.

Compound **2b** *(X = Cl):* Compound **1b** (X = Cl, 25.0 mg, 0.06 mmol) in $DCCl_3$ (0.8 ml) was irradiated at 10°C for 2 h. MPC (PE/EtOAc, 3:1) yielded **2b** (X = Cl, 22 mg, 88%) as a colourless solid, mp 190–192°C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2030, 2860 (C–H). – UV (CH_3CN): λ_{max} (lg ε) = 310 (3.47), 299 (3.64), 288 (3.59). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91, 0.95 (2 s, 6H, 16-*exo*, -*endo*-CH_3), 1.10 (s, 6H, 1-, 10-CH_3), 2.01 (AB, 2H, 13-H_2, J_{AB} = 11.6 Hz), 2.79 (t, 2H, 11-, 15-H, *J* = 2.4 Hz), 3.15 (m_c, 2H, 12H, 14-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.31 (q, CH_3-1, -10), 17.84, 22.90 (2 q, 16-CH_3), 36.55 (t, C-13), 52.20 (d), 54.20 (d), 54.56 (s, C-16), 57.84 (d), 79.30, 79.36 (2 s, C-1, -10, -3, -8), 126.82, 129.64 (2 s, C-4, -5, -6, -7). – MS (70 eV): *m/z* (%) = 407.8 (0.50), 406.8 (0.50), 405.8 (2.57), 404.8 (1.06), 403.8 (5.23), 402.7 (0.86), 401.8 (4.06) [M^+, Cl isotopes], 122.1 (100). – $C_{18}H_{18}Cl_4N_2$ (404.2): calcd. C 53.49, H 4.49, N 6.93; found C 53.87, H 4.42, N 6.95.

Compound **4b** *(sat.):* Compound **3b** (sat., 25 mg, 0.10 mmol) in $CDCl_3$ (0.6 ml) were irradiated at –15°C for 3 h. Filtration through a pad of silica gel (EtOAc, then MeOH) yielded a crude product (28 mg). Sublimation (115°C, 0.05 Torr) afforded **4b** (sat. 12 mg, 48%) as a colourless solid, mp 176–178°C. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 269 (3.36), 262 (3.35). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14, 1.20 (2 s, 6H, 17-*exo*,*endo*-CH_3), 1.41–1.49 (m, 2H), 1.67 (s, 2H), 1.71–1.80 (m, 2H), 2.73 (m_c, 2H), 3.07 (s, 2H, 1-, 10-H), 5.51 (m_c, 2H), 6.08 (m_c, 2H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.73 (t, C-13, -14), 20.28, 22.05 (2 q, CH_3-*endo*-, *exo*-17), 38.27 (d), 45.92 (s, C-17), 46.06 (d), 68.23 (s, C-3, -8), 74.65 (d, C-1, -10), 125.80, 126.98 (2 d, C-4, -5, -6, -7). – MS (70 eV): *m/z* (%) = 252.1 (22.11) [M^+], 224.1 (3.27) [$M^+ - N_2$], 130.1 (100). – $C_{17}H_{20}N_2$ (252.4): calcd. C 80.91, H 7.99, N 11.10; found C 80.90, H 8.24, N 11.26.

Compound **4c**: Compound **3d** (12.0 mg, 0.04 mmol) in $DCCl_3$ (0.6 ml) was irradiated at –15°C for 4.5 h. After filtration through a pad of silica gel (EtOAc) **4c** (10 mg, 83%) was obtained as a colourless powder, dec. 182–183°C. – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3050 (=C–H). – UV (CH_3CN): λ_{max} (lg ε) = 261 (3.40). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25, 1.27 (2 s, 6H, 3-*exo*-,*endo*-CH_3), 2.79 (m_c, 2H), 3.24 (s, 2H), 3.41 (s, 2H, 2a-, 4-H), 5.63–5.66 (m, 2H), 5.79–5.82 (m, 2H, 10-, 11-, 12-, 13-H), 7.22–7.24 (m, 4-, 6-, 7-, 8-, 9-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.25, 22.07 (2 q, CH_3-*exo*-,*endo*-3), 48.94 (d), 49.15 (d), 49.64 (s, C-3), 71.25 (s, C-9c, -13a), 74.76 (d, C-2a, -4), 125.92 (d), 126.11 (d, 4 C), 126.93 (d), 135.81 (s, C-5a, -9a). – MS (70 eV): *m/z* (%) = 300.0 (29.82), 178.1 (100). – $C_{21}H_{20}N_2$ (300.0): calcd. C 83.96, H 6.72, N 9.32, found C 84.15, H 6.73, N 8.99.

[*] Dedicated to Prof. Dr. *J. Sauer* on the occasion of his 65th birthday.

[1] Part XXII: U. Brand, S. Hünig, H.-D. Martin, B. Mayer, *Liebigs Ann.*, submitted (LA 96070).

[2] Partly taken from the Ph.D. thesis of K. Beck, University of Würzburg, **1980**.

[3] U. Brand, Ph.D. thesis, University of Würzburg, **1990**.

[4] B. Albert, W. Berning, C. Burschka, S. Hünig, F. Prokschy, *Chem. Ber.* **1984**, *117*, 1465–1475.

[5] K. Beck, S. Hünig, *Chem. Ber.* **1987**, *120*, 477–483.

[6] S. Hünig, P. Kraft, *J. Pakt. Chem.* **1990**, *332*, 133–142.

[7] S. Hünig, P. Kraft, F.-G. Klärner, U. Artschwager-Perl, K. Peters, H. G. von Schnering, *Liebigs Ann. Chem.* **1995**, 351–156.

[8] H. E. Ungnade, E. T. McBee, *Chem. Rev.* **1958**, *58*, 249–320.

[9] J. S. Newcomer, E. T. McBee, *J. Am. Chem. Soc.* **1949**, *71*, 946–951.

[10] H. F. Zimmerman, G. L. Grunewald, R. M. Paufler, *Org. Synth.* **1966**, *46*, 101–104.

[11] M. S. Raasch, *J. Org. Chem.* **1980**, *45*, 856–867.

[12] K. Beck, S. Hünig, F.-G. Klärner, U. Artschwager-Perl, *Chem. Ber.* **1987**, *120*, 2041–2051.

[13] M. K. Anwer, A. F. Spatola, *Tetrahedron Lett.* **1985**, *26*, 1381–1384.

[14] Preliminary communication: K. Beck, S. Hünig, *Angew. Chem.* **1986**, *98*, 193–194; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 187–188.

[15] K. Beck, A. Höhn, S. Hünig, F. Prokschy, *Chem. Ber.* **1984**, *117*, 517–533.

[16] The trimeric azine **29** constitutes another derivative of 4,5-dihydropyridazine (cf. ref.[18]).

[17] K. Alder, F. Paschen, H. Vogt, *Chem. Ber.* **1942**, *12*, 1501–1514.

[18] S. Hünig, F. Prokschy, *Chem. Ber.* **1984**, *117*, 534–553.

[19] G. Fischer, E. Beckmann, H. Prinzbach, G. Rihs, J. Wirz, *Tetrahedron Lett.* **1986**, *27*, 1273–1276.

[20] [20a] M. T. Reetz, *Angew. Chem.* **1972**, *84*, 161–163; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 129–131. – [20b] M. T. Reetz, *Tetrahedon* **1973**, *29*, 2189–2194. – [20c] M. T. Reetz, *Adv. Organomet. Chem.* **1977**, *16*, 33–65.

[21] R. B. Woodward, R. Hoffmann, *The Conversation of Orbital Symmetry*, VCH, Weinheim, **1970**.

[22] M. Korat, D. Ginsburg, *Tetrahedron* **1973**, *29*, 2373–2381.

[23] [23a] K. Mackenzie, *J. Chem. Soc.* **1965**, 4646–4653. – [23b] J. A. K. Howard, K. Mackenzie, R. E. Johnson, *Tetrahedron Lett.* **1989**, *30*, 5005–5008.

[24] K. Mackenzie, E. C. Gravett, R. J. Gregory, J. A. K. Howard, J. P. Maher, *Tetrahedron Lett.* **1992**, *33*, 5629–5632 and literature cited therein.

[25] For definition of domino or tandem reactions cf. L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *32*, 131–164; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–164. – L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136.

[26] [26a] See ref.[4]. – [26b] S. Hünig, H.-D. Martin, B. Mayer, K. Peters, F. Prokschy, H. G. von Schnering, *Chem. Ber.* **1987**, *120*, 195–201. – [26c] S. Hünig, M. Schmitt, *Liebigs Ann.* **1995**, 1801–1805. – [26d] S. Hünig, M. Schmitt, *Liebigs Ann.*, **1996**, 559–573. – [26e] S. Hünig, M. Schmitt, *Liebigs Ann.*, **1996**, 575–583.

[27] K. Beck, S. Hünig, G. Kleefeld, H.-D. Martin, K. Peters, F. Prokschy, H. G. von Schnering, *Chem. Ber.* **1986**, *119*, 543–553.

[28] Available amount of **2a** (system **1**, $5_C/6_N$) were too small for PE investigations.

[29] R. C. Bingham, M. J. S. Dewar, D. H. Lo, *J. Am. Chem. Soc.* **1975**, *97*, 1285–1294.

[30] B. Albert, W. Berning, Ch. Burschka, S. Hünig, H.-D. Martin, F. Prokschy, *Chem. Ber.* **1981**, *114*, 423–432.

[31] M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **1977**, *99*, 4899–4906, 4907–4912.

[32] F. Brogli, E. Giovannini, E. Heilbronner, R. Schurter, *Chem. Ber.* **1973**, *106*, 961–969.

[33] M. J. Mirbach, K. Liu, M. F. Mirbach, W. R. Cherry, N. J. Turro, P. S. Engel, *J. Am. Chem. Soc.* **1978**, *100*, 5122–5129.

[34] P. S. Engel, C. Steel, *Accounts Chem. Res.* **1973**, *6*, 275–281.

[35] N. J. Turro, J. Liu, H. D. Martin, M. Kunze, *Tetrahedron Lett.* **1980**, *21*, 1299–1302.

[36] M. J. Goldstein, R. Hoffmann, *J. Am. Chem. Soc.* **1971**, *93*, 6193–6204. – See also ref.[26b].

[37] W. C. Still, M. Kalm, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

[38] G. Helmchen, B. Glatz, *Ein apparativ einfaches System und Säulen höchster Trennleistung zur präparativen Mitteldruckchromatography*, Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart, **1978**.

[39] Futher details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404990 (**1**) and -404989 (**3a**).

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