Synthesis, Structure and Reactivity of Cyclopenta-annulated 1,2,3,4-Tetrazines☆

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The 2-aryl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazines **3a**–**n** are formed by coupling of the diazocyclopentadienes **1a** and **1b** with arenediazonium salts and subsequent reversible electrocyclization of the primary coupling products **2a**–**n**. From the solutions of the equilibrium mixtures of **2a** ⇌ **3a** – **2n** ⇌ **3n** the tetrazines **3a**–**d**, **h**–**k** and the arylazo-diazocyclopentadienes **2e**–**g** and **2l**–**n** crystallize. The 2-methyl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazines **3o** and **3p** are obtained by addition of methyllithium to **1a** and **1b** followed by a diazo transfer reaction and cyclization. In solutions of **3o** and **3p** the ring-opened isomers **2o** and **2p** could not be detected. X-ray analyses of **3h** and **3p** prove their bicyclic planar geometry in the solid state. ^{15}N-NMR and temperature-dependent ^{1}H-NMR spectroscopy have enabled a detailed study of the reversible ring closure reaction in the case of **2d** ⇌ **3d**. Reaction of 2-phenyl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3b**) with tetrafluoroboric acid results in the formation of the protonated monocyclic salt **4**. Furthermore **3b** undergoes electrophilic substitution reactions preferably at C-7, as demonstrated by bromination, formylation, and trifluoroacetylation. Photolysis of solutions of **2i/3i**, **2k/3k**, and **2l/3l** leads to the ketene imines **11a**–**c**. The structure of **11c** has been determined by X-ray crystallography.

During the last decades attempts to understand the nature and the causes of heteroaromaticity led to a rule of thumb, that the cyclic conjugation of π-electron systems will be disturbed but not cancelled by replacement of a methine group by nitrogen or a vinylene group by oxygen, sulfur, or a nitrogen-containing group. In search of the limits of this concept unsaturated heterocycles comprising a maximum of heteroatoms have attracted the attention of chemists for a long time and still remain a subject of wide interest. In this context 1,2,3,4-tetrazines constitute a field of increasing importance. As first representatives of a six-membered ring system with four adjacent nitrogen atoms tetrahydro-1,2,3,4-tetrazines were synthesized by Kreher and Wißmann[1] in 1971 and shortly afterwards by Nelson and Fibinger[2] as well as by Seebach et al.[3]. In marked contrast to these hydrogenated derivatives, fully unsaturated 1,2,3,4-tetrazines seem to be less readily accessible. To our knowledge, only two groups have reported on unambiguous preparations of 1,2,3,4-tetrazines so far. In 1988 Ohsawa et al.[4] generated an unstable triazolo-annulated 1,2,3,4-tetrazine, and in 1991 Tartakovskii et al.[5] achieved the synthesis of some benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxides. Extensive theoretical investigations of polyazines[6] focus on the study of stability, geometry, and aromaticity.

In order to study the influence of heteroatoms in the π perimeter on the bonding character and reactivity of novel heterocyclic π-electron systems[7] we have generated the stable 2-aryl- and 2-alkyl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazines **3a**–**p**[8,9] using the diazocyclopentadienes **1a** and **1b** as building blocks. In this paper we report on the formation, structure, and reactions of the new heterocycles **3a**–**p**.

For the formation of the 2-aryltetrazines **3a**–**n**, the diazocyclopentadienes **1a** and **1b** are converted into the arylazo-diazocyclopentadienes **2a**–**n** by reaction with arenediazonium salts in aqueous methanol or in acetonitrile. The primary coupling products **2a**–**n** spontaneously undergo a reversible 10 π electrocyclization, which leads to the cyclopenta[*e*]tetrazines **3a**–**n**. The reversibility of the ring closure reaction of **2a/3a**–**2n/3n** in solution allows the observation of the equilibrium between the bond isomers **2** and **3**. As the ratios indicate (Table of Scheme 1), the equilibrium between **2** and **3** strongly depends on the nature of the substituents in positions 2, 5, and 7. Steric as well as electronic effects are responsible for this. Comparison of the values for compounds **2c/3c**, **2d/3d**, **2e/3e** with those of **2j/3j**, **2k/3k**, **2l/3l** shows the influence of the bulky *tert*-butyl groups in the 5- and 7-position of the tetrazines **3**. They exert a buttressing effect and favor the bicyclic structures **3**. In contrast, a substituent in *o*-position of the 2-aryl group shifts the equilibrium towards the monocyclic isomers **2** (**2b/3b** vs. **2d/3d**, **2c/3c** vs. **2f/3f**, **2i/3i** vs. **2k/3k** or **2j/3j** vs. **2m/3m**). The *o*-substituent forces the aryl group of the plane of the heterocycle and consequently lowers the conjugation between the two π systems. The electron-attracting effect of nitro groups (**2b/3b** vs. **2c/3c**; **2d/3d** vs. **2e/3e**, **2f/3f**, and **2g/3g**; **2i/3i** vs. **2j/3j**; or **2k/3k** vs. **2l/3l**, **2m/3m**, and **2n/3n**) increases the equilibrium concentration of the azodiazo isomers **2**, due to a more effective resonance stabilization. As

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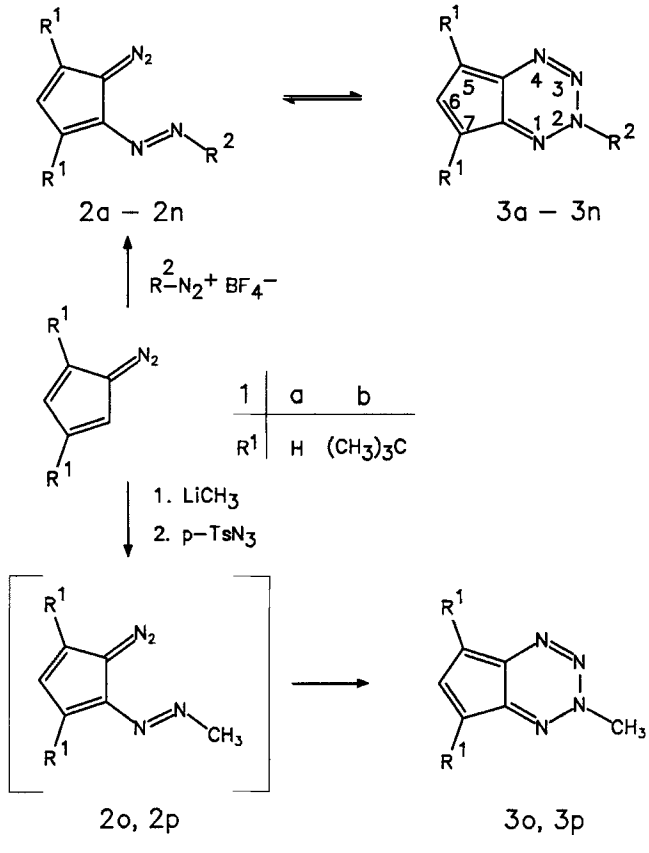
a consequence of this equilibrium, the reaction of the diazocyclopentadienes **1a** and **1b** with 4-methoxybenzene-, benzene-, 4-nitrobenzene-, and *o*-toluenediazonium salts results in the isolation of the deeply colored crystalline tetrazines **3a–d** and **3h–k**, whereas the use of 2-methyl-5-nitrobenzene-, 2-methyl-4-nitrobenzene-, and 2,4-dinitrobenzenediazonium tetrafluoroborate leads to the likewise crystalline and intensively colored diazocyclopentadienes **2e–g** and **2l–n**.

Scheme 1. Synthesis of **2/3**; ratio of the bond isomers **2** ⇌ **3** in $CDCl_3$ solution in dependence of the substituents



Comp.	R^1	R^2	**2**:**3**[a]
2a/3a	H	4-$CH_3OC_6H_4$	<2[b]:>98
2b/3b	H	C_6H_5	3 : 97
2c/3c	H	4-$NO_2C_6H_4$	13 : 87
2d/3d	H	2-$CH_3C_6H_4$	23 : 77
2e/3e	H	2-CH_3-5-$NO_2C_6H_3$	88 : 12
2f/3f	H	2-CH_3-4-$NO_2C_6H_3$	94 : 6
2g/3g	H	2,4-$(NO_2)_2C_6H_3$	>98 : <2[b]
2h/3h	$C(CH_3)_3$	4-$CH_3OC_6H_4$	<2[b]:>98
2i/3i	$C(CH_3)_3$	C_6H_5	<2[b]:>98
2j/3j	$C(CH_3)_3$	4-$NO_2C_6H_4$	5 : 95
2k/3k	$C(CH_3)_3$	2-$CH_3C_6H_4$	7 : 93
2l/3l	$C(CH_3)_3$	2-CH_3-5-$NO_2C_6H_3$	43 : 57
2m/3m	$C(CH_3)_3$	2-CH_3-4-$NO_2C_6H_3$	96 : 4
2n/3n	$C(CH_3)_3$	2,4-$(NO_2)_2C_6H_3$	>98 : <2[b]
2o/3o	H	–	0 : 100
2p/3p	$C(CH_3)_3$	–	0 : 100

[a] Ratio evaluated from ^{1}H-NMR integrals. – [b] Cannot be observed any more by means of ^{1}H-NMR spectroscopy and is therefore assumed to be less than 2%.

The azodiazo-tetrazino isomerism may be the reason why Cram and Partos[10], who performed the reaction of diazocyclopentadiene **1a** with benzenediazonium tetrafluoroborate as early as 1963, assigned only structure **2b** to the isolated product. Their conclusion was mainly based on the diazo absorption band in the IR spectrum of the adduct dissolved in chloroform. This band is due to a small equilibrium concentration of **2b** (Scheme 1) and could not be observed by us in a solid-state IR spectrum (KBr disc).

The 2-methyltetrazines **3o** and **3p** are accessible in reasonable yield by reaction of the diazocyclopentadienes **1a** and **1b**, respectively, with methyllithium followed by a diazo transfer reaction using tosyl azide[11]. Presumably, the alkylazo-diazocyclopentadienes **2o** and **2p** are first formed and cyclize immediately after their generation to the 2-methyl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazines **3o** and **3p**. In contrast to the aryl-substituted species **2a/3a–2n/3n**, for solutions of **3o** and **3p** no indication of the presence of the diazocyclopentadienes **2o** and **2p** has been obtained by IR- and NMR-spectroscopic investigations.

X-ray analyses of a triclinic crystal of 5,7-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3h**)[8,12] and a monoclinic crystal of 5,7-di-*tert*-butyl-2-methyl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3p**)[9,12] both prove the planar geometry of the bicyclic systems.

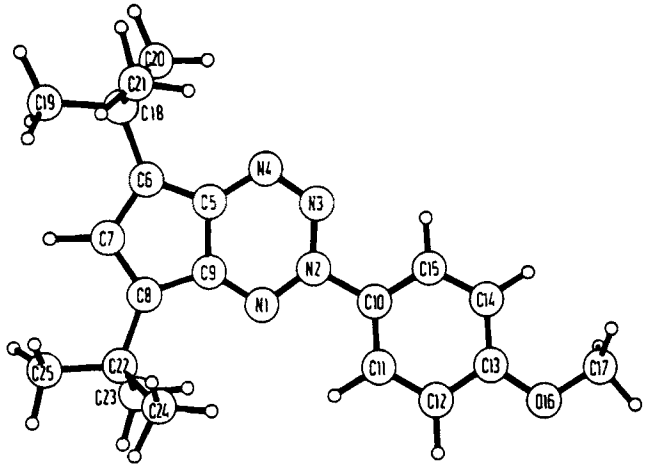


Figure 1. Crystal structure of 5,7-di-*tert*-butyl-2-(4-methoxyphenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3h**). The numbering of the atoms does not correspond to the nomenclature. Selected bond lengths: N1–N2 1.320(8) Å, N2–N3 1.363(8), N3–N4 1.300(8), N4–C5 1.359(9), C5–C9 1.455(9), C5–C6 1.378(10), C6–C7 1.421(9), C7–C8 1.381(9), C8–C9 1.409(9), C9–N1 1.305(8)

The C–C bond lengths of the π perimeter of **3h** and **3p** have been found to range between 1.374 and 1.428 Å and are in good accordance with other structures containing a five-membered carbocycle as part of an aromatic bicycle (e.g. azulene[13] and pseudoazulenes[14]). The lengths of the central bonds of **3h** and **3p**, which are the longest in the bicyclic compounds (1.46–1.47 Å), are also similar to those of corresponding π-electron systems[13,14]. In the six-membered rings the N–N distances (1.300 to 1.363 Å) prove to be not very different and are in between the range of the typical values for localized N–N single and double bonds (N–N = 1.449, N=N = 1.252 Å). Hence X-ray crystal-

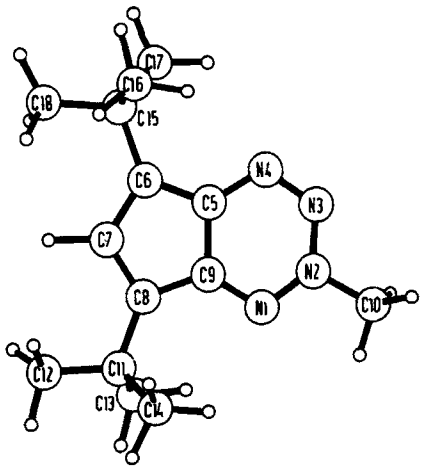


Figure 2. Crystal structure of 5,7-di-*tert*-butyl-2-methyl-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3p**). The numbering of the atoms does not correspond to the nomenclature. Selected bond lengths: N1–N2 1.328(2) Å, N2–N3 1.358(2), N3–N4 1.300(2), N4–C5 1.344(2), C5–C9 1.472(2), C5–C6 1.374(2), C6–C7 1.428(2), C7–C8 1.385(2), C8–C9 1.412(2), C9–N1 1.312(2)

lography corroborates the aromatic nature of the cyclopenta[*e*]-1,2,3,4-tetrazines **3a** to **3p**, as it does for 6-phenyl-[1,2,3]triazolo[4,5-*e*]-1,2,3,4-tetrazine[4].

^{15}N-NMR spectroscopy is a direct and potent method for studying the azodiazo-tetrazino isomerism. The equilibrium mixture of the 2-tolyltetrazine system **2d** ⇌ **3d** at 20°C in DMSO proves to be a particularly useful example. The equilibrium ratio of **2d**:**3d** = 1:4 allows the observation and distinction of both isomers. Whereas the four resonances of **2d** appear in the ^{15}N-NMR spectrum in the ranges typical of azo and diazo nitrogen atoms[15] an assignment for the signals of N-1 to N-4 of the new heterocycle **3d** based on chemical shifts is possible only for the pyrrole-like nitrogen N-2, which causes the signal at highest field. Polarization transfer experiments (DEPT) cannot be used to assign the resonances because of the lack of J(N,H) couplings. However, samples of **3b** and **3d** labelled with ^{15}N in position 1 and 4, respectively (see Experimental) enable the signal assignment illustrated in Figure 3.

Though ^{1}H-NMR spectroscopic investigations cannot prove the position of the four nitrogen atoms directly, the chemical shifts of the signals of the protons of the five-membered ring allow a distinction to be made between the isomers **2d** and **3d**. The resonance line for 3-H of **2d** is detected at δ = 6.20, and thus 3-H shows olefinic character. However, 6-H of the corresponding tetrazine **3d** gives rise to a signal at δ = 8.19. All other cyclopenta[*e*]-1,2,3,4-tetrazine/arylazo-diazocyclopentadiene mixtures **2/3** of which both isomers are detectable by ^{1}H-NMR spectroscopy show similar characteristics. Hence the chemical shifts support the existence of a diamagnetic ring current for the bicyclic systems **3**.

The analysis of temperature-dependent ^{1}H-NMR spectra of a DMF solution of **2d/3d** reveals a clear preference of the ring-opened structure **2d** at high temperatures. This is in accordance with the expected influence of the entropy on the equilibrium. For the process **2d** ⇌ **3d** a free activation energy of $\Delta G^{\neq}$ (333 K) = 72.1 ± 1 kJ/mol has been determined by line-shape analysis[16].

Like many other hetero analogues[14] of azulene also the 2*H*-cyclopenta[*e*]-1,2,3,4-tetrazines **3** display not only bonding and NMR features but also UV/Vis spectra (see Experimental) remarkably similar to those of the parent hydrocarbon. Concerning their chemical reactivity pseudoazulenes are known to undergo protonation[17] and electro-

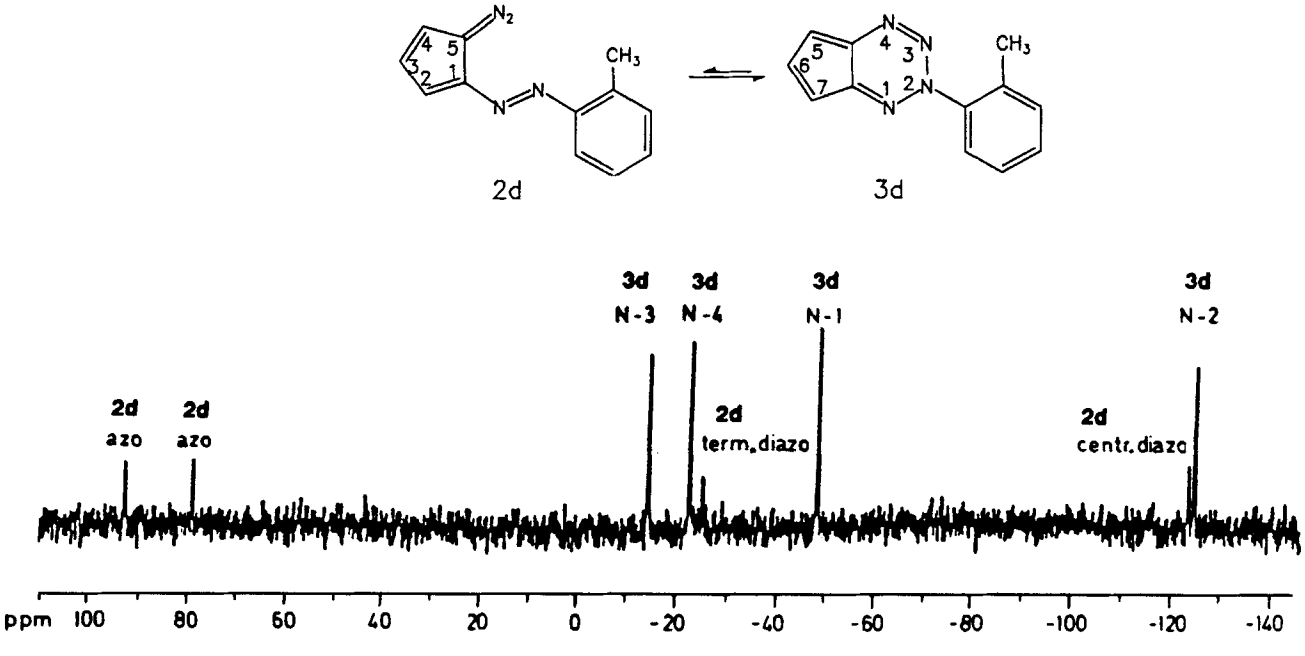
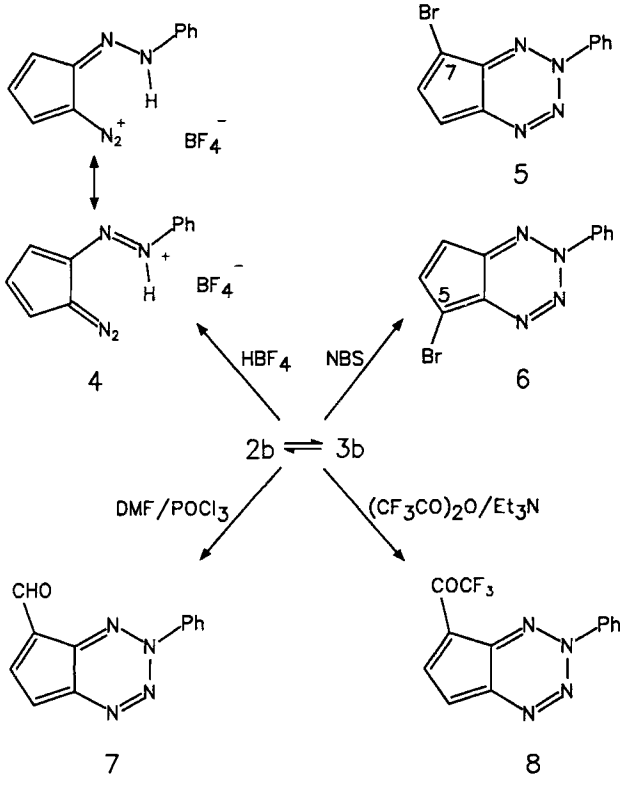


Figure 3. 40.5-MHz ^{15}N-NMR spectrum of a 1.3 M solution of **2d** ⇌ **3d** in [D$_6$]DMSO

philic substitution[18] in positions 5 and 7 which correspond to the 1- and 3-position of azulene.

Scheme 2. Reactions of **2b/3b**



However, treatment of the 2-phenyltetrazine **3b** with tetrafluoroboric acid yields the ring-opened salt **4** as dark brown crystals in nearly quantitative yield. The unstable compound decomposes upon heating and in solution already at room temperature. The IR spectrum of **4** exhibits an intense absorption at 2185 cm^{-1}, which demonstrates the existence of a ring-opened structure with a diazonium salt-like character.

Reaction of **3b** with *N*-bromosuccinimide in acetonitrile furnishes a mixture of the 7- and the 5-bromocyclopenta[*e*]-1,2,3,4-tetrazine **5** and **6**. The regioisomers can be separated by column chromatography on silica gel and are obtained as pure crystalline solids in yields of 38 and 20%, respectively. Solutions of **5** and **6** in chloroform at room temperature contain 10 and 3% of the corresponding ring-opened azodiazo isomer. Structural assignment is made by means of NMR spectroscopy on the basis of ^1H-^1H and ^1H-^{13}C coupling constants. The ^1H-NMR spectrum of the dominant isomer **5** exhibits with ^3J(5-H,6-H) = 3.2 Hz a smaller coupling constant than **6** does with ^3J(6-H,7-H) = 4.9 Hz. This indicates a formal single bond between C-5 and C-6 of **5** and a short, formal double bond between C-6 and C-7 of **6**. Further confirmation is obtained by a gated-decoupled ^{13}C-NMR experiment. This allows a clear distinction between the two isomers by observation of the signals of C-7a of **5** (δ = 134.5) and **6** (δ = 138.3). Whereas the signal of C-7a of **5** appears as a triplet caused by ^3J(C-7a,5-H) ≈ 7 and ^3J(C-7a,6-H) ≈ 9 Hz, the signal of C-7a of **6** is a doublet of doublets caused by ^3J(C-7a,6-H) = 12.1 and ^2J(C-7a,7-H) = 3.7 Hz.

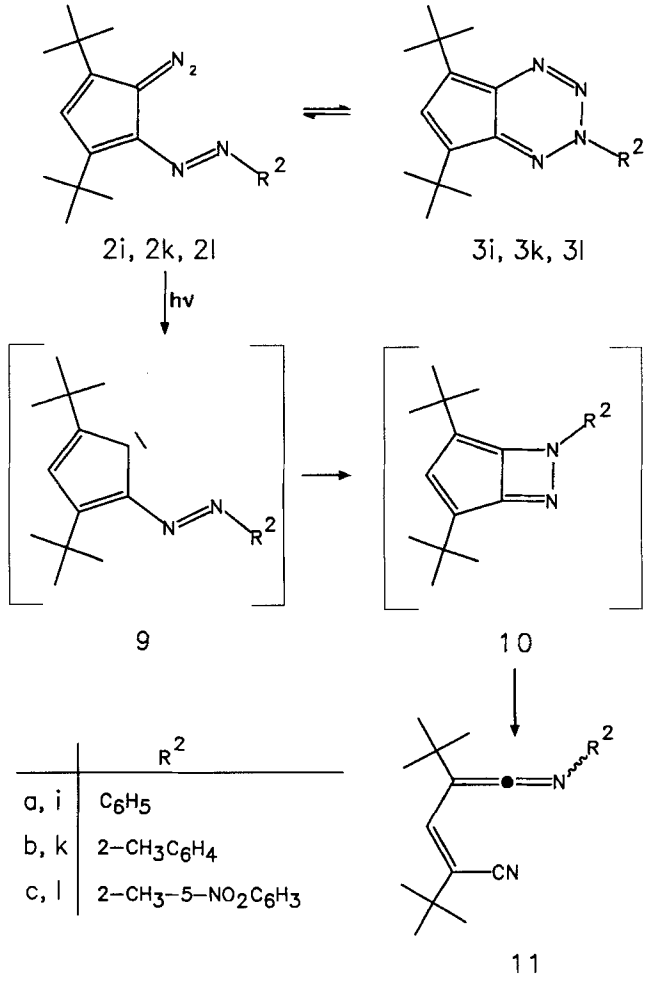
Formylation of **3b** under Vilsmeier conditions takes place only in the 7-position with the formation of **7**, which is obtained as red crystals. The equilibrium concentration of the azodiazo isomer of **7** in chloroform at room temperature is assumed to be less than 2%, as only the IR but not the NMR spectrum of **7** shows absorptions corresponding to the monocyclic structure.

Treatment of the phenyltetrazine **3b** with trifluoroacetic anhydride yields the 7-trifluoroacetyl derivative **8** as dark red crystalls in a yield of 31%. The monocyclic isomer of **8** cannot be detected by IR- and NMR-spectroscopic investigations carried out in chloroform at room temperature.

The preferred substitution at C-7 of the 2-phenyltetrazine **3b** by electrophilic reagents is in accordance with the behavior of pseudoazulenes containing a pyrrole-like nitrogen in the 2-position of the six-membered ring[14,18]. A significant influence of an electron-attracting substituent in the 5- or 7-position of **3b** on the azodiazo-tetrazino isomerism has not been observed.

On the other hand, photolysis of the equilibrium mixtures of **2i/3i**, **2k/3k**, and **2l/3l** is dominated by the reactivity of the diazo group of the ring-opened structures. Ir-

Scheme 3. Photolysis of **2i/3i**, **2k/3k**, and **2l/3l**



radiation of solutions of these compounds with a mercury vapor lamp at 18°C leads to the ketene imines **11a–c** in yields up to 79% as yellow crystals. The structural assignment of **11** is carried out by X-ray crystallography of a single crystal of **11c**[12]. The ketene imine **11c** crystallizes in the triclinic space group $P\bar{1}$ with 2 formula units in the unit cell. Its butadiene subunit shows *Z* configuration with a dihedral angle of 32° resulting in a slightly distorted U-shape of the molecule backbone.

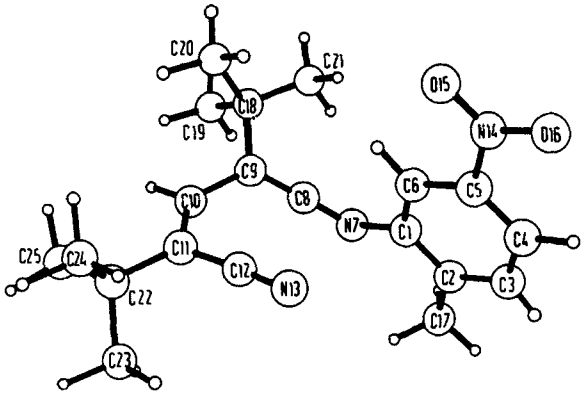


Figure 4. Crystal structure of (*Z*)-5-*tert*-butyl-2,2-dimethyl-6-(2-methyl-5-nitrophenylimino)-3,5-hexadiene-3-carbonitrile (**11c**). The numbering of the atoms does not correspond to the nomenclature. Selected bond lengths and angles: C1–N7 1.425(3) Å, N7–C8 1.223(3), C8–C9 1.310(3), C9–C10 1.462(3), C10–C11 1.333(3), C11–C12 1.438(3), C12–N13 1.144(3), C1–N7–C8 123.5(2)°, C8–C9–C10–C11 32.3(5)°

The formation of the α,β-unsaturated ketene imines **11** starts presumably with a photoinduced loss of nitrogen. Intramolecular stabilization of the resulting cyclopentadienylidene fragments **9** may result in the formation of the bicyclic intermediates **10**, which finally are transformed into the isolated ketene imines **11** by a formal [2 + 2] cycloreversion. Due to the known instability of aldoketene imines, by photolysis of **2b/3b** the corresponding imine could not be isolated.

The described properties of the cyclopenta[*e*]-1,2,3,4-tetrazines **3** clearly show that 1,2,3,4-tetrazines embedded in a suitable 10 π-electron system display an unexpectedly high stability. This is very likely caused by the substituted pyrrole-like nitrogen in the tetrazine moiety of **3**, which leads to a structural relationship with tetrazoles[19] as well as 1,2,3-triazoles[20] and accounts for the observed azodiazo-tetrazino isomerism. In spite of a significant influence of the nitrogen atoms on bonding character and reactivity of cyclic conjugated systems, a comparison of spectroscopic data and X-ray structure analyses of **3** with those of the isoelectronic azulene indicates an aromatic character of the cyclopenta[*e*]-1,2,3,4-tetrazines **3**.

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Experimental

NMR: Bruker WM 300, AC 300, ARX 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz, ^{15}N: 30.4 MHz), Bruker AMX 400 (^{15}N: 40.5 MHz). ^{1}H- and ^{13}C-NMR spectra were measured with TMS as internal standard. The ^{15}N-NMR data refer to nitromethane as external standard. – MS: Finnigan MAT 311-A/100 MS. – IR: Beckman IR 5A, Perkin-Elmer 125. – UV: Beckman DK-2A, UV 5240. – Column chromatography: basic alumina [activity BII–III (Brockmann) ICN Biomedicals] and silica gel [70–230 mesh (ASTM) Macherey-Nagel]. – Melting points: Kofler apparatus (Reichert, Vienna, Austria). – The *diazonium tetrafluoroborates*[21] and *diazocyclopentadiene* (**1a**)[11] were prepared as described. For ^{15}N labelling experiments sodium [^{15}N]nitrite [ICL (Massachusetts)] was used, and the same synthetical routes as for the non-labelled compounds were applied.

1) *General Procedure for the Synthesis of* **2a/3a–2g/3g**: A cooled solution of 0.92 g (10.0 mmol) of diazocyclopentadiene (**1a**) in 20 ml of methanol was added to 10.0 mmol of the appropriate arenediazonium tetrafluoroborate dissolved or suspended in aqueous methanol at 0°C, and the resulting mixture was stirred for 10 min to 3 h at this temperature. For the isolation of **2a/3a**, **2b/3b**, and **2d/3d** the reaction mixture was added to 200 ml of ice cold water and extracted several times with diethyl ether. The combined organic solutions were washed neutral with water and dried with magnesium sulfate. The solvent was evaporated in vacuo at 30°C, and the residue was purified by column chromatography with *n*-hexane/diethyl ether (9:1) on alumina B II–III. For the isolation of **2c/3c**, **2e/3e**, **2f/3f**, and **2g/3g** the reaction mixture was filtered, washed once with a small amount of cold diethyl ether and recrystallized from methanol or *n*-hexane.

2-(4-Methoxyphenyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3a**): Violet crystals, yield 11%, m.p. 106°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (vw, C–H), 1590 (m), 1490 (s). – Solutions of **3a** in chloroform at room temp. contained a small equilibrium concentration of 5-diazo-1-(4-methoxyphenylazo)-1,3-cyclopentadiene (**2a**), which could only be detected by IR spectroscopy. Thus, a ratio of **2a**:**3a** ≈ 2:98 or less was assumed. – IR ($CHCl_3$): $\tilde{\nu}$ = 2950 cm^{-1} (w, C–H), 2110 (m, CNN, **2a**), 1600 (s), 1490 (s). – UV (*n*-hexane): λ_{max} (lg ε): 248 nm (4.15), 253 (4.15), 261 (4.10) sh, 325 (4.31), 367 (3.87) sh, 387 (3.64) sh, 441 (3.33), 451 (3.32), 468 (3.29), 487 (3.24), 506 (3.15), 527 (3.06), 549 (2.92), 575 (2.78), 601 (2.46), 632 (2.20). – ^{1}H NMR ($CDCl_3$) **3a**: δ = 3.88 (s, 3H, CH_3), 7.05 (m_c, 3H, 2 aryl-H and 5- or 7-H), 7.17 (dd, ^3J = 3.3, ^4J = 0.7 Hz, 1H, 5- or 7-H), 8.17 (m_c, 3H, 2 aryl-H and 6-H). – ^{13}C NMR ($CDCl_3$) **3a**: δ = 55.5 (OCH_3), 106.0 (C-7 or C-5), 107.1 (C-5 or C-7), 114.4 (aryl-CH), 121.9 (aryl-CH), 126.4 (C-4a), 137.1 (C_{quat}), 136.6 (C_{quat}), 145.6 (C-6), 159.9 (C_{quat}). – MS (70 eV), *m/z* (%): 226 (42) [M^+], 183 (40) [$M^+ - C_3H_7$], 77 (100) [$C_6H_5^+$]. – $C_{12}H_{10}N_4O$ (226.2): calcd. C 63.71, H 4.35, N 24.76; found C 63.92, H 4.35, N 24.60.

2-Phenyl-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3b**): Deep violet needles, yield 21%, m.p. 91°C (ethanol/water). – IR (KBr): $\tilde{\nu}$ = 1582 cm^{-1} (w), 1540 (w), 1490 (m). – Solutions of **3b** in chloroform at room temp. contained 3% (from ^{1}H-NMR integrals) of 5-diazo-1-(phenylazo)-1,3-cyclopentadiene (**2b**). – IR ($CHCl_3$): $\tilde{\nu}$ = 3030 cm^{-1} (w, sh, C–H), 2970 (m), 2100 (m, CNN, **2b**), 1587 (m), 1540 (m), 1490 (m). – UV (*n*-hexane): λ_{max} (lg ε): 239 nm (3.94), 251 (3.97), 277 (4.20), 304 (4.32), 351 (3.74) sh, 358 (3.71) sh, 367 (3.68) sh, 378 (3.57) sh, 387 (3.46) sh, 427 (3.08), 438 (3.10), 452 (3.10), 466 (3.09), 483 (3.07), 505 (3.02), 525 (2.96), 546 (2.83), 572 (2.69), 598 (2.35), 628 (2.10). – ^{1}H NMR ($CDCl_3$) **3b**: δ = 7.06 (dd, ^3J = 4.6, ^4J = 0.7 Hz, 1H, 7-H), 7.19 (dd, ^3J = 3.5, ^4J = 0.7

Hz, 1H, 5-H), 7.44 (m_c, 1H, *p*-Ph-H), 7.56 (m_c, 2H, *m*-Ph-H), 8.12 (dd, ^3J = 4.6, ^3J = 3.5 Hz, 1H, 6-H), 8.23 (m_c, 2H, *o*-Ph-H). – ^{1}H NMR ($CDCl_3$) **2b**: δ = 6.16 (br. s, 3-H), 6.86 (br. s, 2H), all other signals were concealed. – ^{13}C NMR ($CDCl_3$) **3b**: δ = 107.2 (C-7), 108.2 (C-5), 120.5 (*o*-Ph-CH), 126.3 (C-4a), 128.9 (*p*-Ph-CH), 129.6 (*m*-Ph-CH), 138.3 (C-7a), 143.8 (C_{quat}), 146.1 (C-6). – ^{15}N NMR (acetone) **3b**: δ = −124.5 (N-2), −57.0 (N-1), −19.43 (N-4 or N-3), −19.03 (N-3 or N-4). – MS (70 eV), *m/z* (%): 196 (34) [M^+], 168 (11) [$M^+ - N_2$], 77 (100) [$C_6H_5^+$]. – $C_{11}H_8N_4$ (196.2): calcd. C 67.37, H 4.11, N 28.55; found C 67.16, H 3.95, N 28.77.

[1-^{15}N]-2-Phenyl-2H-cyclopenta[e]-1,2,3,4-tetrazine (20% ^{15}N) has been prepared from **1a** and terminal ^{15}N-labelled benzenediazonium tetrafluoroborate[23]. – ^{15}N NMR (acetone): δ = −57.0 (N-1). – MS (70 eV), *m/z* (%): 196/197 (30/13) [M^+], 168/169 (10/4) [$M^+ - N_2$], 77 (100) [$C_6H_5^+$].

2-(4-Nitrophenyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3c**): Brownish crystals, yield 74%, m.p. 180°C (dec., methanol). – IR (KBr): $\tilde{\nu}$ = 1585 cm^{-1} (m), 1560 (w), 1513 (m). – Solutions of **3c** in chloroform at room temp. contained 13% (from ^{1}H-NMR integrals) of 5-diazo-1-(4-nitrophenylazo)-1,3-cyclopentadiene (**2c**). – IR ($CHCl_3$): $\tilde{\nu}$ = 2100 cm^{-1} (m, CNN, **2c**), 1585 (m), 1558 (w), 1515 (m). – UV (dioxane): λ_{max} (lg ε): 267 nm (4.15), 328 (4.34), 376 (3.99), 397 (3.83), 461 (3.50), 568 (2.86) sh, 622 (2.22) sh. – ^{1}H NMR ($CDCl_3$) **3c**: δ = 7.16 (d, ^3J = 4.6 Hz, 1H, 7-H), 7.33 (d, ^3J = 3.0 Hz, 1H, 5-H), 8.18 (dd, ^3J = 4.6, ^3J = 3.0 Hz, 1H, 6-H), 8.48 (m_c, 4H, aryl-H). – ^{1}H NMR ($CDCl_3$) **2c**: δ = 6.30 (br. s, 1H, 3-H), 7.00 (br. s, 1H, 2- or 4-H), 7.06 (br. s, 1H, 2- or 4-H), 7.86 (br. s, 2H, aryl-H), 8.33 (br. s, 2H, aryl-H). – MS (70 eV), *m/z* (%): 241 (81) [M^+], 76 (100). – $C_{11}H_7N_5O_2$ (241.2): calcd. C 54.77, H 2.92, N 29.03; found C 54.72, H 2.86, N 28.83.

2-(o-Tolyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3d**): Purple crystals, yield 27%, m.p. 55–56°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 1541 cm^{-1} (w), 1517 (w), 1490 (m), 1453 (m), 1408 (s). – Solutions of **3d** in chloroform at room temp. contained 23% (from ^{1}H-NMR integrals) of 5-diazo-1-(*o*-tolylazo)-1,3-cyclopentadiene (**2d**). – IR ($CHCl_3$): $\tilde{\nu}$ = 2100 cm^{-1} (s, CNN, **2d**), 1538 (vw), 1515 (w), 1490 (m), 1458 (m), 1406 (m). – UV (*n*-hexane): λ_{max} (lg ε): 267 nm (4.26), 292 (4.22), 340 (3.88) sh, 424 (3.69), 541 (2.55) sh, 566 (2.24) sh, 593 (1.86) sh, 624 (1.61). – ^{1}H NMR ($CDCl_3$) **3d**: δ = 2.31 (s, 3H, CH_3), 7.07 (dd, ^3J = 4.8, ^4J = 0.9 Hz, 1H, 7-H), 7.24 (dd, ^3J = 3.5, ^4J = 0.9 Hz, 1H, 5-H), 7.49 (m_c, 3H, aryl-H), 7.74 (m_c, 1H, aryl-H), 8.19 (dd, ^3J = 4.8, ^3J = 3.5 Hz, 1H, 6-H). – ^{1}H NMR ($CDCl_3$) **2d**: δ = 2.48 (s, 3H, CH_3), 6.20 (dd, ^3J = 5.0, ^3J = 3.2 Hz, 1H, 3-H), 6.90 (m_c, 2H, 2- and 4-H), 7.27 (m_c, 3H, aryl-H), 7.69 (m_c, 1H, aryl-H). – ^{15}N NMR ([D_6]DMSO) **3d**: δ = −124.9 (N-2), −48.4 (N-1), −22.7 (N-4), −14.5 (N-3). – ^{15}N NMR ([D_6]DMSO) **2d**: δ = −123.6 (centr. CNN), −25.3 (term. CNN), +79.2 (N=N), +93.0 (N=N). – MS (70 eV), *m/z* (%): 210 (40) [M^+], 91 (100) [$C_7H_7^+$]. – $C_{12}H_{10}N_4$ (210.2): calcd. C 68.56, H 4.79, N 26.65; found C 68.29, H 4.69, N 26.89.

Solutions of *[4-^{15}N]-2-(o-Tolyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (20% ^{15}N)* prepared from *o*-toluenediazonium tetrafluoroborate and centrally ^{15}N-labelled diazocyclopentadiene **1a**[23] in chloroform at room temp. contained 23% of the ring-opened isomer. – ^{15}N NMR ([D_6]DMSO): δ = −122.7 (centr. CNN of ^{15}N-**2d**), −21.7 (N-4 of ^{15}N-**3d**). – MS (70 eV), *m/z* (%): 210/211 (64/36) [M^+], 91 (100) [$C_6H_4CH_3$].

5-Diazo-1-(2-methyl-5-nitrophenylazo)-1,3-cyclopentadiene (**2e**): Maroon crystals, yield 63%, m.p. 165°C (dec., *n*-hexane). – IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1} (w, C–H), 2100 (s, CNN), 1600 (w), 1587 (w), 1504 (m). – Solutions of **2e** in chloroform at room temp. contained 12% (from ^{1}H-NMR integrals) of 2-(2-methyl-5-nitrophenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3e**). – UV (dichloromethane): λ_{max} (lg ε): 269 nm (4.42), 287 (4.29) sh, 355 (4.02), 440 (3.97). – ^{1}H NMR ($CDCl_3$) **3e**: δ = 2.50 (s, 3H, CH_3), 7.14 (br. d, ^3J = 4.0 Hz, 1H, 5-H or 7-H), 7.32 (br. s, 1H, 5- or 7-H), 7.62 (br. m_c, 1H, aryl-H), 8.24 (br. dd, $^3J \approx 4$, $^3J \approx 4$ Hz, 1H, 6-H), 8.31 (br. m_c, 1H, aryl-H), 8.51 (br. s, 1H, aryl-H). – ^{1}H NMR ($CDCl_3$) **2e**: δ = 2.56 (s, 3H, CH_3), 6.28 (dd, ^3J = 5.0, ^3J = 3.5 Hz, 1H, 3-H), 7.02 (m_c, 2H, 2- and 4-H), 7.43 (m_c, 1H, aryl-H), 8.09 (m_c, 1H, aryl-H), 8.54 (m_c, 1H, aryl-H). – MS (70 eV), *m/z* (%): 255 (80) [M^+], 51 (100). – $C_{12}H_9N_5O_2$ (255.2): calcd. C 56.47, H 3.55, N 27.44; found C 56.31, H 3.39, N 27.55.

5-Diazo-1-(2-methyl-4-nitrophenylazo)-1,3-cyclopentadiene (**2f**): Brownish crystals, yield 38%, m.p. 145°C (dec., *n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2080 cm^{-1} (s, CNN), 1580 (w), 1490 (m). – Solutions of **2f** in chloroform at room temp. contained 6% (from ^{1}H-NMR integrals) of 2-(2-methyl-4-nitrophenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3f**). – UV (dioxane): λ_{max} (lg ε): 273 nm (4.24), 295 (4.09), 366 (4.05), 458 (4.04). – ^{1}H NMR ($CDCl_3$) **2f**: δ = 2.45 (s, 3H, CH_3), 6.29 (m_c, 1H, 3-H), 7.01 (m_c, 1H, 2- or 4-H), 7.05 (m_c, 1H, 2 or 4-H), 7.78 (m_c, 1H, aryl-H), 8.07 (m_c, 1H, aryl-H), 8.20 (m_c, 1H, aryl-H). – ^{1}H NMR ($CDCl_3$) **3f**: δ = 7.11 (br. s, 5- or 7-H), 7.20 (br. s, 5- or 7-H), 8.25 (br. m_c, aryl-H), all other signals were concealed. – MS (70 eV), *m/z* (%): 255 (100) [M^+], 227 (15) [$M^+ - N_2$]. – $C_{12}H_9N_5O_2$ (255.2): calcd. C 56.47, H 3.53, N 27.44; found C 56.49, H 3.42, N 27.52.

5-Diazo-1-(2,4-dinitrophenylazo)-1,3-cyclopentadiene (**2g**): Brownish crystals, yield 41%, m.p. 135°C (dec., *n*-hexane). – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} (w, C–H), 2105 (s, CNN), 1585 (m), 1480 (s), 1412 (m). – In solutions of **2g** in chloroform at room temp. 2-(2,4-dinitrophenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3g**) could not be detected. Thus, a ratio of **2g**:**3g** ≈ 98:2 or larger was assumed. – UV (*n*-hexane): λ_{max}: 243 nm sh, 248, 255, 262 sh, 266 sh, 269, 273 sh, 293 sh, 378, 473. – ^{1}H NMR ($CDCl_3$): δ = 6.36 (t, ^3J = 4.7, ^3J = 3.5 Hz, 1H, 3-H), 7.12 (dd, ^3J = 3.5, ^4J = 2.0 Hz, 1H, 2-H), 7.19 (dd, ^3J = 4.7, ^4J = 2.0 Hz, 1H, 4-H), 8.01 (m_c, 1H, aryl-H), 8.42 (m_c, 1H, aryl-H), 8.66 (m_c, 1H, aryl-H). – MS (70 eV), *m/z* (%): 286 (74) [M^+], 119 (40) [$M^+ - C_6H_3N_2O_4$], 93 (100). – $C_{11}H_6N_6O_4$ (286.2): calcd. C 46.16, H 2.11, N 29.36; found C 45.70, H 2.00, N 28.30.

2) *1,3-Di-tert-butyl-5-diazo-1,3-cyclopentadien* (**1b**)[22]: A solution of 1.78 g (10.0 mmol) of 1,3-di-*tert*-butyl-1,3-cyclopentadiene in 25 ml of dry *n*-hexane was added to 7 ml (10.0 mmol) of a boiling 1.5 M solution of *n*-butyllithium in *n*-hexane and 1.12 g (10.0 mmol) of tmeda. After heating for 2 h the reaction mixture was cooled to −15°C, and a solution of 1.97 g (10.0 mmol) of tosyl azide in 50 ml of dry THF was added slowly. While warming to room temp. the reaction mixture was stirred for 16 h, then 200 ml of a 2 N KOH solution was added, and the mixture was stirred for another 30 min. The organic phase was diluted by 300 ml of diethyl ether, washed neutral with water, dried with magnesium sulfate, and then the solvent was evaporated in vacuo at 20°C. Chromatography of the dark red residue on alumina with *n*-pentane yielded after evaporation of the solvent 1.98 g (97%) of a 1:3 mixture (from ^{1}H-NMR integrals) of 1,4- and 1,3-di-*tert*-butyl-5-diazo-1,3-cyclopentadiene as a red oil. Further purification and elemental analysis was not carried out for security reasons. The mixture was used for the following preparations. – IR (film): $\tilde{\nu}$ = 2100 cm^{-1} (s, CNN), 2130 (s, CNN). – UV (*n*-hexane): λ_{max}: 299 nm. – ^{1}H NMR ($CDCl_3$) **1b**: δ = 1.17 [s, 9H, $C(CH_3)_3$], 1.26 [s, 9H, $C(CH_3)_3$], 5.73 (d, ^4J = 2.5 Hz, 1H, 2-H or 4-H), 6.31 (d, ^4J = 2.5 Hz, 1H, 2-H or 4-H). – ^{1}H NMR ($CDCl_3$) of 1,4-di-*tert*-butyl-5-diazo-1,3-

cyclopentadiene: δ = 1.25 [s, 18H, $C(CH_3)_3$], 5.54 (s, 2H, 2-H and 3-H). – MS (70 eV), *m/z* (%): 204 (50) [M^+], 176 (23) [$M^+ - N_2$], 161 (100).

3) *General Procedure for the Synthesis of* **2h/3h–2n/3n**: A solution of 2.04 g (10.0 mmol) of 1,3-di-*tert*-butyl-5-diazo-1,3-cyclopentadiene (**1b**) in 20 ml of acetonitrile was added to 10.0 mmol of the appropriate arenediazonium tetrafluoroborate dissolved or suspended in acetonitrile at 0°C. The resulting mixture was stirred at 20°C for 10 min to 19 h. The dark reaction mixture was poured into icecold water and extracted once with diethyl ether. The organic phase was washed with water and dried with magnesium sulfate. The solvent was evaporated in vacuo at 30°C, and the residue was purified by column chromatography with *n*-hexane/diethyl ether (9:1) on alumina B II–III.

5,7-Di-tert-butyl-2-(4-methoxyphenyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3h**): Black needles, yield 14%, m.p. 117°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (s, C–H), 1505 (s). – Solutions of **3h** in chloroform at room temp. contained a small equilibrium concentration of 2,4-di-*tert*-butyl-5-diazo-1-(4-methoxyphenylazo)-1,3-cyclopentadiene (**2h**), which could only be detected by IR spectroscopy. Thus, a ratio of **2h**:**3h** ≈ 2:98 or less was assumed. – IR ($CHCl_3$): $\tilde{\nu}$ = 3040 cm^{-1} (w, C–H), 2900 (s, C–H), 2080 (w, CNN, **2h**), 1600 (m), 1492 (s), 1458 (s). – UV (*n*-hexane): λ_{max} (lg ε): 244 nm (4.09), 275 (4.05) sh, 329 (4.37), 380 (3.88) sh, 497 (3.05) sh, 521 (3.06), 560 (3.02) sh, 610 (2.81) sh. – ^{1}H NMR ($CDCl_3$): δ = 1.55 [s, 9H, $C(CH_3)_3$], 1.59 [s, 9H, $C(CH_3)_3$], 3.89 (s, 3H, CH_3), 7.04 (m_c, 2H, aryl-H), 7.75 (s, 1H, 6-H), 8.12 (m_c, 2H, aryl-H). – ^{15}N NMR (acetone): δ = –134.0 (N-2), –59.8 (N-1), –29.4 (N-3 or N-4), –18.7 (N-4). – MS (70 eV), *m/z* (%): 338 (35) [M^+], 295 (100) [$M^+ - C_3H_7$], 77 (58) [$C_6H_5^+$], 57 (68) [$C(CH_3)_3^+$]. – $C_{20}H_{26}N_4O$ (338.5): calcd. C 70.97, H 7.74, N 16.56; found C 71.01, H 7.88, N 16.42.

5,7-Di-tert-butyl-2-phenyl-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3i**): Deep violet needles, yield 33%, m.p. 119°C (ethanol/diethyl ether). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w, C–H), 2960 (s, C–H), 1590 (m), 1555 (m), 1530 (m). – Solutions of **3i** in chloroform at room temp. contained a small equilibrium concentration of 2,4-di-*tert*-butyl-5-diazo-1-(phenylazo)-1,3-cyclopentadiene (**2i**), which could only be detected by IR spectroscopy. Thus, a ratio of **2i**:**3i** ≈ 2:98 or less was assumed. – IR ($CHCl_3$): $\tilde{\nu}$ = 3050 cm^{-1} (w, C–H), 2900 (s, C–H), 2080 (w, CNN, **2i**), 1590 (m), 1563 (w), 1534 (w). – UV (*n*-hexane): λ_{max} (lg ε): 238 nm (3.96), 280 (4.17), 313 (4.35), 384 (3.76), 399 (3.68) sh, 500 (2.94) sh, 524 (2.96), 557 (2.92) sh, 608 (2.72) sh. – ^{1}H NMR ($CDCl_3$): δ = 1.55 [s, 9H, $C(CH_3)_3$], 1.59 [s, 9H, $C(CH_3)_3$], 7.39 (m_c, 1H, *p*-Ph-H), 7.54 (m_c, 2H, *m*-Ph-H), 7.75 (s, 1H, 6-H), 8.22 (m_c, 2H, *o*-Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 31.3 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$], 33.0 [$C(CH_3)_3$], 33.2 [$C(CH_3)_3$], 119.3 (*o*-Ph-CH), 120.1 (C-4a), 127.6 (*p*-Ph-CH), 129.4 (*m*-Ph-CH), 131.3 (C-7), 131.9 (C-5), 136.7 (C-7a), 139.8 (C-6), 143.7 (*i*-Ph-C). – ^{15}N NMR (acetone): δ = –135.3 (N-2), –59.4 (N-1), –27.7 (N-3), –17.9 (N-4). – MS (70 eV), *m/z* (%): 308 (40) [M^+], 265 (98) [$M^+ - C_3H_7$], 77 (100) [$C_6H_5^+$], 57 (44) [$C(CH_3)_3^+$]. – $C_{19}H_{24}N_4$ (308.4): calcd. C 73.99, H 7.84, N 18.17; found C 74.24, H 8.05, N 17.97.

5,7-Di-tert-butyl-2-(4-nitrophenyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3j**): Deep violet crystals, yield 35%, m.p. 154–159°C (ethanol/diethyl ether). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w, C–H), 2980 (s, C–H), 1610 (w), 1590 (m), 1565 (m), 1540 (m), 1512 (s). – Solutions of **3j** in chloroform at room temp. contained 5% (from ^{1}H-NMR integrals) of 2,4-di-*tert*-butyl-5-diazo-1-(4-nitrophenylazo)-1,3-cyclopentadiene (**2j**). – IR ($CHCl_3$): $\tilde{\nu}$ = 3077 cm^{-1} (vw, C–H), 2920 (m, C–H), 2090 (w, CNN, **2j**), 1590 (s), 1567 (m, sh), 1517 (s), 1490 (s). – UV (*n*-hexane): λ_{max} (lg ε): 270 nm (4.14), 334 (4.38), 342 (4.37) sh, 397 (4.05), 415 (3.97), 484 (3.38). – ^{1}H NMR ($CDCl_3$) **3j**: δ = 1.56 [s, 9H, $C(CH_3)_3$], 1.59 [s, 9H, $C(CH_3)_3$], 7.74 (s, 1H, 6-H), 8.38 (br. s, 4H, aryl-H). – ^{1}H NMR ($CDCl_3$) **2j**: δ = 6.33 (s, 3-H), all other signals were concealed. – ^{13}C NMR ($CDCl_3$) **3j**: δ = 31.0 [$C(CH_3)_3$], 31.4 [$C(CH_3)_3$], 33.2 [$C(CH_3)_3$], 33.4 [$C(CH_3)_3$], 118.7 (CH), 122.6 (C_{quat}), 125.2 (CH), 133.9 (C_{quat}), 135.9 (C_{quat}), 139.1 (C_{quat}), 140.5 (C-6), 146.2 (C_{quat}), 147.7 (C_{quat}). – ^{15}N NMR (toluene) **3j**: δ = –137.9 (N-2), –58.3 (N-1), –23.1 (N-3, N-4 or NO_2), –11.7 (N-3, N-4 or NO_2), –10.4 (N-3, N-4 or NO_2). – MS (70 eV), *m/z* (%): 353 (39) [M^+], 310 (83) [$M^+ - C_3H_7$], 57 (85) [$C(CH_3)_3^+$]. – $C_{19}H_{23}N_5O_2$ (353.5): calcd. C 64.57, H 6.56, N 19.81; found C 64.60, H 6.59, N 20.02.

5,7-Di-tert-butyl-2-(o-tolyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine (**3k**): Violet crystals, yield 34%, m.p. 82°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2900 (s, C–H), 1450 (m), 1388 (w), 1359 (m). – Solutions of **3k** in chloroform at room temp. contained 7% (from ^{1}H-NMR integrals) of 2,4-di-*tert*-butyl-5-diazo-1-(*o*-tolylazo)-1,3-cyclopentadiene (**2k**). – IR ($CHCl_3$): $\tilde{\nu}$ = 2900 cm^{-1} (s, C–H), 2080 (s, CNN, **2k**), 1450 (m), 1389 (w), 1362 (s). – UV (*n*-hexane): λ_{max} (lg ε): 273 nm (4.22), 295 (4.22), 370 (3.79), 443 (3.46). – ^{1}H NMR ($CDCl_3$) **3k**: δ = 1.50 [s, 9H, $C(CH_3)_3$], 1.61 [s, 9H, $C(CH_3)_3$], 2.41 (s, 3H, CH_3), 7.38 (m_c, 3H, aryl-H), 7.57 (m_c, 1H, aryl-H), 7.79 (s, 1H, 6-H). – ^{1}H NMR ($CDCl_3$) **2k**: δ = 1.33 [br. s, 9H, $C(CH_3)_3$], 2.47 (br. s, 3H, CH_3), 5.94 (br. s, 1H, 3-H), all other signals were concealed. – ^{13}C NMR ($CDCl_3$) **3k**: δ = 18.8 (CH_3), 31.4 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$], 32.9 [$C(CH_3)_3$], 33.1 [$C(CH_3)_3$], 119.4 (C_{quat}), 126.2 (CH), 126.7 (CH), 128.9 (CH), 130.5 (C_{quat}), 130.6 (C_{quat}), 131.6 (aryl-CH), 133.2 (C_{quat}), 135.8 (C_{quat}), 139.5 (C-6), 143.6 (C_{quat}). – MS (70 eV), *m/z* (%): 322 (38) [M^+], 279 (100) [$M^+ - C_3H_7$], 91 (77) [$C_7H_7^+$], 57 (33) [$C(CH_3)_3^+$]. – $C_{20}H_{26}N_4$ (322.3): calcd. C 74.53, H 8.13, N 17.38; found C 74.40, H 8.17, N 17.67.

2,4-Di-tert-butyl-5-diazo-1-(2-methyl-5-nitrophenylazo)-1,3-cyclopentadiene (**2l**): Red crystals, yield 44%, m.p. 184–187°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1} (m, C–H), 2080 (s, CNN), 1582 (w), 1510 (m), 1470 (m). – Solutions of **2l** in chloroform at room temp. contained 57% (from ^{1}H-NMR integrals) of 5,7-di-*tert*-butyl-2-(2-methyl-5-nitrophenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3l**). – UV (*n*-hexane): λ_{max} (lg ε): 233 nm (4.15), 272 (4.27), 295 (4.11), 375 (3.67), 449 (3.72). – ^{1}H NMR ([D_5]pyridine) **2l** at –30°C: δ = 1.28 [s, 9H, $C(CH_3)_3$], 1.64 [s, 9H, $C(CH_3)_3$], 2.49 (s, 3H, CH_3), 6.28 (s, 1H, 3-H), 7.47 (m_c, 1H, aryl-H), 8.22 (m_c, 1H, aryl-H), 8.72 (m_c, 1H, aryl-H). – ^{1}H NMR ([D_5]pyridine) **3l** at –30°C: δ = 1.62 [s, 9H, $C(CH_3)_3$], 1.76 [s, 9H, $C(CH_3)_3$], 2.42 (s, 3H, CH_3), 7.52 (m_c, 1H, aryl-H), 8.19 (s, 1H, 6-H), 8.31 (m_c, 1H, aryl-H), 8.83 (m_c, 1H, aryl-H). – MS (70 eV), *m/z* (%): 367 (56) [M^+], 324 (100) [$M^+ - C_3H_7$], 57 (73) [$C(CH_3)_3^+$]. – $C_{20}H_{25}N_5O_2$ (367.5): calcd. C 65.37, H 6.86, N 19.06; found C 65.65, H 6.86, N 19.10.

2,4-Di-tert-butyl-5-diazo-1-(2-methyl-4-nitrophenylazo)-1,3-cyclopentadiene (**2m**): Red crystals, yield 32%, m.p. 120°C (dec., *n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (m, C–H), 2080 (s, CNN), 1590 (w), 1538 (m), 1492 (m), 1453 (m). – Solutions of **2m** in chloroform at room temp. contained 4% (from ^{1}H-NMR integrals) of 5,7-di-*tert*-butyl-2-(2-methyl-4-nitrophenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3m**). – UV (*n*-hexane): λ_{max} (lg ε): 245 nm (3.91), 285 (4.04), 378 (4.34), 412 (4.27). – ^{1}H NMR ($CDCl_3$) **2m**: δ = 1.32 [s, 9H, $C(CH_3)_3$], 1.62 [s, 9H, $C(CH_3)_3$], 2.72 (s, 1H, CH_3), 6.29 (s, 1H, 3-H), 7.53 (m_c, 1H, aryl-H), 8.05 (m_c, 1H, aryl-H), 8.15 (m_c, 1H, aryl-H). – ^{1}H NMR ($CDCl_3$) **3m**: δ = 2.50 (br. s, CH_3), all other signals were concealed. – ^{13}C NMR ($CDCl_3$) **2m**: δ = 17.8 (CH_3), 29.6 [$C(CH_3)_3$], 32.3 [$C(CH_3)_3$], 33.0 [$C(CH_3)_3$], 36.4

[$C(CH_3)_3$], 74.8 (CNN), 106.0 (CH), 116.2 (CH), 121.9 (CH), 126.3 (CH), 137.6 (C_{quat}), 143.9 (C_{quat}), 144.0 (C_{quat}), 147.1 (C_{quat}), 148.3 (C_{quat}), 155.1 (C_{quat}). – MS (70 eV), *m/z* (%): 367 (31) [M^+], 57 (100) [$C(CH_3)_3^+$]. – $C_{20}H_{25}N_5O_2$ (367.5): calcd. C 65.37, H 6.86, N 19.06; found C 65.30, H 6.85, N 19.18.

2,4-Di-tert-butyl-5-diazo-1-(2,4-dinitrophenylazo)-1,3-cyclopentadiene (**2n**): Deep green needles, yield 45%, m.p. 177–179°C (ethanol/diethyl ether). – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} (vw, C–H), 2900 (m, C–H), 2100 (s, CNN), 1590 (m), 1515 (m), 1426 (w). – In solutions of **2n** in chloroform at room temp. 5,7-di-*tert*-butyl-2-(2,4-dinitrophenyl)-2*H*-cyclopenta[*e*]-1,2,3,4-tetrazine (**3n**) could not be detected. Thus, a ratio of **2n**:**3n** ≈ 98:2 or larger was assumed. – UV (*n*-hexane): λ_{max} (lg ε): 257 nm (4.08), 281 (4.20), 307 (4.01) sh, 416 (4.08), 506 (4.28). – ^1H NMR ($CDCl_3$): δ = 1.35 [s, 9H, $C(CH_3)_3$], 1.48 [s, 9H, $C(CH_3)_3$], 6.11 (br. s, 1H, 3-H), 7.90 (m_c, 1H, aryl-H), 8.38 (m_c, 1H, aryl-H), 8.60 (m_c, 1H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ = 29.3 [$C(CH_3)_3$], 32.2 [$C(CH_3)_3$], 34.3 [$C(CH_3)_3$], 35.3 [$C(CH_3)_3$], 117.8 (CH), 118.3 (CH), 120.0 (CH), 127.0 (CH), 142.5 (C_{quat}), 144.7 (2 × C_{quat}), 145.4 (C_{quat}), 149.6 (C_{quat}), 157.1 (C_{quat}), 158.3 (C_{quat}). – MS (70 eV), *m/z* (%): 398 (12) [M^+], 57 (78) [$C(CH_3)_3^+$], 41 (100). – $C_{19}H_{22}N_6O_4$ (398.4): calcd. C 57.28, H 5.57, N 21.09; found C 57.11, H 5.44, N 21.22.

4) *Synthesis of 2-Methyl-2H-cyclopenta[e]-1,2,3,4-tetrazine* (**3o**): 21 ml (20.0 mmol) of a 0.95 M solution of methyllithium in dry diethyl ether was added under nitrogen at −10°C to a solution of 1.84 g (20.0 mmol) of diazocyclopentadiene (**1a**) in 75 ml of dry diethyl ether. After the mixture had been stirred for 30 min a solution of 3.94 g (20.0 mmol) of tosyl azide in 60 ml of dry diethyl ether was added at the same temp. After the cooling had been removed the reaction mixture was stirred for another 2 h and poured into 500 ml of 2 N KOH. The mixture was then stirred for 15 min, 500 ml of diethyl ether was added, and after filtration through Celite the phases were separated. The aqueous solution was extracted three times with 300 ml of diethyl ether, the combined organic phases were washed neutral with water, dried with magnesium sulfate, the solvent was removed in vacuo at 30°C and the residue purified by column chromatography with *n*-hexane/diethyl ether (6:4) on silica gel. The first fraction contained a small amount of **1a**. The following violet fraction yielded 0.30 g (11%) of **3o** as violet crystals, m.p. 68°C (sublimation). – IR ($CHCl_3$): $\tilde{\nu}$ = 2940 cm^{-1} (w), 1587 (w), 1410 (s). – UV (*n*-hexane): λ_{max} (lg ε): 255 nm (4.44), 271 (4.22) sh, 322 (3.23) sh, 328 (3.28) sh, 335 (3.34) sh, 342 (3.38), 350 (3.43), 357 (3.36), 367 (3.37), 425 (2.23) sh, 440 (2.33) sh, 455 (2.41) sh, 471 (2.47), 488 (2.51), 506 (2.50), 526 (2.47), 547 (2.35), 572 (2.23), 598 (1.91), 628 (1.67). – ^1H NMR ($CDCl_3$): δ = 4.57 (s, 3H, CH_3), 6.95 (dd, ^3J = 4.5, ^4J = 1.0 Hz, 1H, 7-H), 7.12 (dd, ^3J = 3.7, ^4J = 1.0 Hz, 1H, 5-H), 8.15 (dd, ^3J = 4.5, ^3J = 3.7 Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 48.8 (CH_3), 104.7 (C-5 or C-7), 105.8 (C-5 or C-7), 127.3 (C-4a or C-7a), 136.9 (C-4a or C-7a), 145.9 (C-6). – ^{15}N NMR (acetone): δ = −130.9 (N-2), −48.9 (N-1), −20.5 (N-3 or N-4), −15.8 (N-4 or N-3). – MS (70 eV), *m/z* (%): 134 (66) [M^+], 119 (38) [$M^+ - CH_3$], 63 (100) [$M^+ - 2\,N_2$]. – $C_6H_6N_4$ (134.1): calcd. C 53.72, H 4.51, N 41.76; found C 53.48, H 4.48, N 41.52.

5) *Synthesis of 5,7-Di-tert-butyl-2-methyl-2H-cyclopenta[e]-1,2,3,4-tetrazine* (**3p**): 10 ml (10.0 mmol) of a 1 M solution of methyllithium in dry diethyl ether was added under nitrogen at −5°C to a solution of 2.04 g (10.0 mmol) of 1,3-di-*tert*-butyl-5-diazo-1,3-cyclopentadiene (**1b**) in 30 ml of dry *n*-hexane. The reaction mixture was allowed to warm up to room temp. and was stirred for 1 h. Then a solution of 1.97 g (10.0 mmol) of tosyl azide in 70 ml of dry THF was added dropwise at 0°C. The mixture was warmed to room temp., stirred for 4 h, poured into icecold water and extracted three times with 100-ml portions of diethyl ether. The combined organic layers were stirred with 500 ml of 2 N KOH and, after separation of the phases, washed neutral with water. The organic solution was dried with magnesium sulfate, and the solvent was removed in vacuo at 30°C. The residue was purified by column chromatography with *n*-hexane/diethyl ether (8:2) on alumina B II–III. The first fraction contained a small amount of **1b**. The following violet fraction yielded 0.15 g (6%) of **3p** as black prisms, m.p. 88°C (*n*-pentane). – IR ($CHCl_3$): $\tilde{\nu}$ = 2900 cm^{-1} (s, C–H), 1590 (vw), 1450 (m), 1389 (m). – UV (dioxane): λ_{max} (lg ε): 264 nm (4.39), 369 (3.55), 377 (3.50) sh, 384 (3.46) sh, 533 (2.44), 553 (2.47) sh. – ^1H NMR ($CDCl_3$): δ = 1.48 [s, 9H, $C(CH_3)_3$], 1.55 [s, 9H, $C(CH_3)_3$], 4.44 (s, 3H, CH_3), 7.78 (s, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 31.2 [2$C(CH_3)_3$], 32.6 [$C(CH_3)_3$], 32.7 [$C(CH_3)_3$], 47.7 (CH_3), 121.2 (C_{quat}), 127.8 (C_{quat}), 128.5 (C_{quat}), 134.1 (C_{quat}), 139.4 (C_{quat}). – ^{15}N NMR (acetone): δ = −141.5 (N-2), −49.5 (N-1), −24.3 (N-3 or N-4), −19.6 (N-4 or N-3). – MS (70 eV), *m/z* (%): 246 (59) [M^+], 57 (50) [$C(CH_3)_3^+$], 41 (100). – $C_{14}H_{22}N_4$ (246.4): calcd. C 68.26, H 9.00, N 22.74; found C 68.44, H 9.05, N 23.03.

6) *X-Ray Structure Analysis of* **3h**: Single crystals were obtained by recrystallization from *n*-hexane. Flat dark violet needles, $C_{20}H_{26}N_4O$, *M* = 338.46, triclinic, space group $P\bar{1}$, *a* = 16.94(2), *b* = 9.622(8), *c* = 6.197(5) Å, α = 107.77(3), β = 92.96(3), γ = 96.64(3)°, *V* = 953.82 Å^3, *Z* = 2, $D_{calcd.}$ = 1.178 g/cm^3, μ = 0.42 cm^{-1} (Mo-K_α). – Measurement of a needle (0.1 × 0.5 × 1.9 mm^3) on a STOE-STADI 4 diffractometer (Mo-K_α radiation, graphite monochromator), cell constant determination by ±ω scan of 60 reflexions with 26.3° < 2θ < 39.3°, 2373 reflexions with 3° < 2θ < 40° were measured ($16 < h < 16$, $8 < k < 9$, $5 < l < 1$), 1447 symmetry-independent reflexions with $|F| > 4\sigma F$. – Structure solution by direct methods (SHELXS-86)[24]. Anisotropic refinement of all carbon atoms, hydrogen atoms positioned, 251 parameters, $w = 3.97/(\sigma^2 F + 0.0041\,F^2)$, *R* = 0.109, R_w = 0.119 (SHELX-76)[25].

7) *X-Ray Structure Analysis of* **3p**: Single crystals were obtained by recrystallization from *n*-pentane. Black prisms, $C_{14}H_{22}N_4$, *M* = 246.36, monoclinic, space group $P2_1/c$, *a* = 12.819(1), *b* = 12.212(1), *c* = 9.640(1) Å, β = 93.30(6)°, *V* = 1506.2 Å^3, *Z* = 4, $D_{calcd.}$ = 1.086 g/cm^3, μ = 0.37 cm^{-1} (Mo-K_α). – Measurement of a prism on an Enraf-Nonius CAD 4 diffractometer (Mo-K_α radiation, graphite monochromator), cell constant determination with 20 reflexions with 5.2° < 2θ < 15.4°, 2051 reflexions with 2° < 2θ < 44° were measured ($0 < h < 13$, $0 < k < 12$, $-10 < l < 10$), 1676 symmetry-independent reflexions with $|F| > 2\sigma F$. – Structure solution by direct methods (SHELXS-86)[24]. Anisotropic refinement of all carbon atoms, hydrogen atoms positioned, 186 parameters, $w = 4.18/(\sigma^2 F + 0.0003\,F^2)$, *R* = 0.0531, R_w = 0.0631 (SHELX–76)[25].

8) *Protonation of* **3b**: 1.5 ml of a solution of tetrafluoroboric acid in diethyl ether (54%) was added slowly to a solution of 1.80 g (9.2 mmol) of **3b** in 360 ml of dry *n*-hexane at room temp. The mixture was stirred for 15 min and filtered. After the precipitate had been washed three times with 30 ml of dry *n*-hexane and dried in vacuo 2.53 g (97%) of diazonium salt **4** was obtained as a dark brown solid, which did not melt below 320°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3215 cm^{-1} (m), 3100 (m, C–H), 2185 (s, CN_2^+), 1605 (w), 1543 (m), 1483 (s), 1061 (br. vs). – UV (dichloromethane): λ_{max}: 273 nm, 304, 364 sh, 516. – ^1H NMR (CD_3CN): δ = 6.93 (dd, ^3J = 4.8, ^3J = 4.1 Hz, 1H, 4-H), 7.37 (dd, ^3J = 4.8, ^4J = 1.5 Hz, 1H, 3- or 5-H), 7.45 (m_c, 1H, Ph-H), 7.56 (m_c, 2H, Ph-H), 7.76 (m_c,

2H, Ph-H), 8.22 (dd, ^3J = 4.1, ^4J = 1.5 Hz, 1H, 3- or 5-H), 12.20 (br. s, 1H, NH). – MS (FD, 0–20 mA), *m/z* (%): 197 (34) [M^+], 196 (100) [$M^+ - H$], 77 (22) [$C_6H_5^+$]. – $C_{11}H_9BF_4N_4$ (284.0): calcd. C 46.52, H 3.19, N 19.73; found C 46.46, H 3.14, N 19.10.

9) *Bromination of* **3b**: To a solution of 0.98 g (5.00 mmol) of **3b** in 25 ml of dry acetonitrile was added slowly a solution of 0.89 g (5.0 mmol) of *N*-bromosuccinimide in 12 ml of dry acetonitrile. After 2 h at room temp. the reaction mixture was poured into ice-cold water and extracted three times with 80 ml of diethyl ether. The combined extracts were dried with magnesium sulfate, and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel with *n*-hexane/diethyl ether (19:1) as eluent. The 5-bromo isomer **6** was eluted first, followed by the 7-bromo isomer **5**.

7-Bromo-2-phenyl-2H-cyclopenta[e]-1,2,3,4-tetrazine (**5**): Deep brown crystals, yield 38%, m.p. 110–111°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 1587 cm^{-1} (vw), 1540 (m), 1477 (s), 1457 (m). – Solutions of **5** in chloroform at room temp. contained 10% of 2-bromo-5-diazo-1-(phenylazo)-1,3-cyclopentadiene (from ^{1}H-NMR integrals). – IR ($CHCl_3$): $\tilde{\nu}$ = 2110 cm^{-1} (s, CNN), 1587 (w), 1540 (m), 1480 (s), 1459 (m, sh). – UV (dioxane): λ_{max} (lg ε): 313 nm (4.34), 374 (3.77), 460 (3.11), 536 (2.99), 592 (2.77). – ^{1}H NMR ($CDCl_3$) **5**: δ = 7.20 (d, ^3J = 3.2 Hz, 1H, 5-H), 7.49 (m_c, 1H, *p*-Ph-H), 7.59 (m_c, 2H, *m*-Ph-H), 8.11 (d, ^3J = 3.2 Hz, 1H, 6-H), 8.29 (m_c, 2H, *o*-Ph-H). – ^{1}H NMR ($CDCl_3$) of ring-opened isomer of **5**: δ = 6.12 (br. s, 3-H), 6.83 (br. s, 4-H), 7.75 (br. s, Ph-H), all other signals were concealed. – GD-^{13}C NMR ($CDCl_3$): δ = 94.5 [d, ^3J(C,5-H) = 8.8 Hz, C-7], 108.0 [dd, ^1J(C,5-H) = 178.4, ^2J(C,6-H) = 3.6 Hz, C-5], 120.5 (dm_c, *m*-Ph-C), 126.9 [d, ^3J(C,6-H) = 10.0 Hz, C-4a], 129.2 (dm_c, *p*-Ph-C), 129.5 (dm_c, *o*-Ph-C), 134.5 [dd, ^3J(C,5-H) ≈ 7, ^3J(C,6-H) ≈ 9 Hz, C-7a], 143.2 (m_c, *i*-Ph-C), 146.2 [dd, ^1J(C,6-H) = 171.7, ^2J(C,5-H) = 4.1 Hz, C-6]. – MS (70 eV), *m/z* (%): 276/274 (20/21) [M^+], 139 (48) [$M^+ - Br - 2\ N_2$], 77 (100) [$C_6H_5^+$]. – $C_{11}H_7BrN_4$ (275.1): calcd. C 48.03, H 2.56, N 20.37; found C 47.89, H 2.45, N 20.35.

5-Bromo-2-phenyl-2H-cyclopenta[e]-1,2,3,4-tetrazine (**6**): Deep brown crystals, yield 20%, m.p. 129–130°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 1538 cm^{-1} (w), 1475 (m), 1451 (m). – Solutions of **6** in chloroform at room temp. contained 3% of 4-bromo-5-diazo-1-(phenylazo)-1,3-cyclopentadiene (from ^{1}H-NMR integrals). – IR ($CHCl_3$): $\tilde{\nu}$ = 2115 cm^{-1} (w, CNN), 1587 (m), 1550 (m), 1480 (m), 1458 (m, sh). – UV (dioxane): λ_{max} (lg ε): 244 nm (4.00), 276 (4.11), 314 (4.31), 374 (3.83), 380 (3.83) sh, 400 (3.68) sh, 485 (3.11), 495 (3.11) sh, 516 (3.08) sh, 538 (3.03) sh, 583 (2.79) sh, 642 (2.19) sh. – ^{1}H NMR ($CDCl_3$): δ = 7.09 (d, ^3J = 4.9 Hz, 1H, 7-H), 7.48 (m_c, 1H, *p*-Ph-H), 7.58 (m_c, 2H, *m*-Ph-H), 8.00 (d, ^3J = 4.9 Hz, 1H, 6-H), 8.23 (m_c, 2H, *o*-Ph-H). – ^{1}H NMR ($CDCl_3$) of ring-opened isomer of **6**: δ = 6.30 (br. s, 2-H), 6.80 (br. s, 3-H), all other signals were concealed. – GD-^{13}C NMR ($CDCl_3$): δ = 97.5 [d, ^3J(C,7-H) ≈ 10 Hz, C-5], 107.8 [dd, ^1J(C,7-H) ≈ 181, ^2J(C,6-H) ≈ 4 Hz, C-7], 120.3 (dm_c, *m*-Ph-C), 123.2 [dd, ^3J(C,6-H) ≈ 8, ^3J(C,7-H) ≈ 5 Hz, C-4a], 129.0 (dm_c, *p*-Ph-C), 129.6 (dm_c, *o*-Ph-C), 138.3 [dd, ^3J(C,6-H) = 12.1, ^2J(C,7-H) = 3.7 Hz, C-7a], 143.3 (m_c, *i*-Ph-C), 146.5 [dd, ^1J(C,6-H) = 168.0, ^2J(C,7-H) = 4.2 Hz, C-6]. – MS (70 eV), *m/z* (%): 276/274 (17/16) [M^+], 139 (77) [$M^+ - Br - 2\ N_2$], 77 (100) [$C_6H_5^+$]. – $C_{11}H_7BrN_4$ (275.1): calcd. C 48.03, H 2.56, N 20.37; found C 48.04, H 2.38, N 20.28.

10) *2-Phenyl-2H-cyclopenta[e]-1,2,3,4-tetrazine-7-carbaldehyde* (**7**): To a solution of 0.98 g (5.00 mmol) of **3b** in 30 ml of dry dichloromethane was added a solution of 0.767 g (5.0 mmol) of phosphorus oxychloride and 3.66 g (50 mmol) of dimethylformamide in 10 ml of dry dichloromethane. After stirring for 1 h at room temp. 200 ml of a 2 N NaOH solution was added, and the mixture was extracted three times with 100 ml of diethyl ether. The combined organic extracts were washed neutral with water, dried with magnesium sulfate, and the solvent was evaporated in vacuo. Chromatography of the residue on alumina with *n*-hexane/diethyl ether (4:1) afforded after evaporation of the solvent 0.09 g (8%) of deep red crystals, m.p. 124–126°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1} (w), 2830 (w), 1655 (s, CO), 1460 (m), 1389 (m). – Solutions of **7** in chloroform contained a small amount of 5-diazo-2-formyl-1-(phenylazo)-1,3-cyclopentadiene, which could only be detected by IR spectroscopy. – IR ($CHCl_3$): $\tilde{\nu}$ = 2930 cm^{-1} (w), 2825 (w), 2120 (w, CNN), 1660 (s, CO), 1460 (m), 1389 (m). – UV (*n*-hexane): λ_{max} (lg ε): 252 nm (4.37), 285 (4.12), 320 (4.30), 370 (3.84) sh, 400 (3.60) sh, 472 (3.36) sh, 486 (3.39), 498 (3.38) sh, 516 (3.35) sh, 537 (3.26) sh, 560 (3.13) sh, 586 (2.84) sh, 613 (2.56) sh. – ^{1}H NMR ($CDCl_3$): δ = 7.28 (d, ^3J = 4.0 Hz, 1H, 5-H), 7.63 (m_c, 3H, Ph-H), 8.35 (m_c, 2H, Ph-H), 8.73 (d, ^3J = 4.0 Hz, 1H, 6-H), 10.46 (s, 1H, CHO). – MS (70 eV), *m/z* (%): 224 (4) [M^+], 196 (50) [M^+ – CO], 77 (100) [$C_6H_5^+$]. – $C_{12}H_8N_4O$ (224.2): calcd. C 64.28, H 3.60, N 24.99; found C 63.52, H 4.40, N 25.02.

11) *2-Phenyl-7-(trifluoroacetyl)-2H-cyclopenta[e]-1,2,3,4-tetrazine* (**8**): To a solution of 0.20 g (1.02 mmol) of **3b** and 0.53 ml (3.82 mmol) of triethylamine in 30 ml of dry dichloromethane was added slowly 0.53 ml (3.81 mmol) of trifluoroacetic anhydride at 0°C. While the reaction mixture was stirred at 20°C further portions of triethylamine (0.53 ml, 3.82 mmol) and trifluoroacetic anhydride (0.53 ml, 3.81 mmol) were added after 2, 24, 65, and 74 h. Then 30 ml of icecold water was added after 90 h, the mixture was stirred for 10 min and extracted three times with 40 ml of diethyl ether. The combined organic extracts were dried with magnesium sulfate, the solvent was evaporated in vacuo, and the remaining residue was chromatographed on silica gel with *n*-hexane/diethyl ether (8:2) as eluent. The starting compound **3b** was eluted first (10 mg, 5%) followed by the 7-trifluoroacetyl derivative **8**. Evaporation of the solvent yielded 90 mg (31%) of dark red crystals, m.p. 128–137°C (dec.). – IR ($CHCl_3$): $\tilde{\nu}$ = 3030 cm^{-1} (w, C–H), 1675 (s, CO), 1595 (w), 1540 (w), 1450 (s). – UV (dioxane): λ_{max} (lg ε): 266 nm (4.35), 329 (4.20), 378 (3.85) sh, 486 (3.57). – ^{1}H NMR ($CDCl_3$): δ = 7.30 (d, ^3J = 4.3 Hz, 1H, 5-H), 7.63 (m_c, 3H, Ph-H), 8.38 (m_c, 2H, Ph-H), 8.82 [dq, ^3J = 4.3, ^5J(F,H) = 1.3 Hz, 1H, 6-H]. – MS (70 eV), *m/z* (%): 292 (18) [M^+], 264 (10) [$M^+ - N_2$], 195 (32) [$M^+ - COCF_3$], 77 (100) [$C_6H_5^+$]. – $C_{13}H_7F_3N_4O$ (292.2): calcd. C 53.49, H 2.41, N 19.17; found C 53.82, H 2.39, N 19.08.

12) *General Procedure for the Photolysis of* **2i/3i**, **2k/3k**, *and* **2l/3l**: A solution of 2 mmol of **2i/3i**, **2k/3k**, or **2l/3l** in *n*-hexane was irradiated (150-W Hg vapor lamp, Original Hanau) at 18°C for 1.5, 2, or 7 h, respectively. The process was accompanied by liberation of nitrogen and decolorization of the originally dark solution. Evaporation of the solvent in vacuo and chromatography of the residue on silica gel yielded the ketene imines **11a–c**.

(Z)-5-tert-Butyl-2,2-dimethyl-6-(phenylimino)-3,5-hexadiene-3-carbonitrile (**11a**): Yellow crystals, yield 77%, m.p. 60°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (m, C–H), 2200 (w, CN), 1980 (s, CCN), 1590 (m). – UV (*n*-hexane): λ_{max}: 237 (4.05) nm, 279 (3.73) sh, 287 (3.85) sh, 308 (4.03). – ^{1}H NMR ($CDCl_3$): δ = 1.20 [s, 9H, $C(CH_3)_3$], 1.21 [s, 9H, $C(CH_3)_3$], 6.37 (s, 1H, 3-H), 7.35 (m_c, 5H, Ph-H). – MS (70 eV), *m/z* (%): 280 (25) [M^+], 265 (100) [$M^+ - CH_3$], 77 (53) [$C_6H_5^+$], 57 (19) [$C(CH_3)_3^+$]. – $C_{19}H_{24}N_2$ (280.4): calcd. C 81.38, H 8.63, N 9.99; found C 81.32, H 8.64, N 10.12.

(Z)-5-tert-Butyl-2,2-dimethyl-6-(o-tolylimino)-3,5-hexadiene-3-carbonitrile (**11b**): Yellow crystals, yield 49%, m.p. 73°C (*n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (m, C–H), 2200 (w, CN), 1975 (s,

CCN), 1580 (m). – UV (*n*-hexane): λ_{max} (lg ε): 239 (4.03) nm, 286 (2.85) sh, 296 (2.98) sh, 312 (4.06). – ^{1}H NMR ($CDCl_3$): δ = 1.20 [s, 9H, $C(CH_3)_3$], 1.21 [s, 9H, $C(CH_3)_3$], 2.43 (s, 3H, CH_3), 6.37 (s, 1H, 3-H), 7.26 (m_c, 4H, aryl-H). – MS (70 eV), *m/z* (%): 294 (26) [M^+], 279 (100) [$M^+ - CH_3$], 91 (27) [$C_7H_7^+$], 57 (14) [$C(CH_3)_3^+$]. – $C_{20}H_{26}N_2$ (294.4): calcd. C 81.58, H 8.90, N 9.51; found C 81.81, H 8.92, N 9.60.

(Z)-5-tert-Butyl-2,2-dimethyl-6-(2-methyl-5-nitrophenylimino)-3,5-hexadiene-3-carbonitrile (**11c**): Yellow plates, yield 79%, m.p. 100°C (methanol). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w, C–H), 2950 (s, C–H), 2190 (m, CN), 1990 (s, CCN), 1590 (m). – UV (*n*-hexane): λ_{max} (lg ε): 232 (4.25) nm, 271 (4.11), 302 (4.09). – ^{1}H NMR ($CDCl_3$): δ = 1.23 [s, 9H, $C(CH_3)_3$], 1.28 [s, 9H, $C(CH_3)_3$], 2.52 (s, 3H, CH_3), 6.42 (s, 1H, 3-H), 7.40 (m_c, 1H, aryl-H), 8.00 (m_c, 1H, aryl-H), 8.13 (m_c, 1H, aryl-H). – MS (70 eV), *m/z* (%): 339 (21) [M^+], 324 (100) [$M^+ - CH_3$], 57 (24) [$C(CH_3)_3^+$]. – $C_{20}H_{25}N_3O_2$ (339.4): calcd. C 70.77, H 7.42, N 12.38; found C 70.35, H 7.52, N 12.30.

13) *X-Ray Structure Analysis of* **11c**: Single crystals were obtained by recrystallization from methanol. Yellow plates, $C_{20}H_{25}N_3O_2$, M = 339.44, triclinic, space group $P\bar{1}$, a = 8.871(1), b = 10.076(1), c = 12.103(1) Å, α = 71.87(1), β = 74.17(1), γ = 79.67(1)°, V = 983.8 Å^3, Z = 2, $D_{calcd.}$ = 1.146 g/cm^3, μ = 0.43 cm^{-1} (Mo-K_α). – Measurement of a plate on an Enraf-Nonius CAD 4 diffractometer (Mo-K_α radiation, graphite monochromator, crystal size 0.58 × 0.53 × 0.23 mm), cell constant determination with 20 reflexions with 4.78° < 2θ < 37.60°, 5480 reflexions with 2° < 2θ < 46° were measured ($-9 < h < 9$, $-11 < k < 11$, $-13 < l < 13$), 2369 symmetry-independent reflexions with $|F| > 4\sigma F$. – Structure solution by direct methods (SHELXS-86)[24]. Anisotropic refinement of all carbon atoms, 3-H, 4-H, 6-H and 10-H found by difference Fourier synthesis, all other hydrogen atoms positioned, 265 parameters, $w = 5.0957/(\sigma^2 F)$, R = 0.0510, R_w = 0.0482 (SHELX-76)[25].

☆ Dedicated to Professor Dr. *Donald J. Cram* on the occasion of his 75th birthday.

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