Cycloaddition of 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to 7-Alkylidene-2,3-benzonorbornadienes

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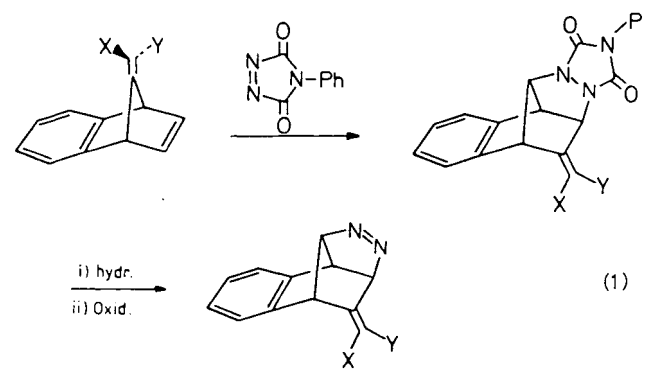
A series of 7-alkylidene-2,3-benzonorbornadienes **2a–f** was prepared from the corresponding fulvenes **1a–f** by reaction with benzyne. The cycloaddition of **2** with PTAD was investigated. While the phenyl derivative **2a** was quite unreactive and afforded traces of the [2 + 2] cycloadduct **3a**, the phenyl methyl system **2b** led to the ene product **3b** in fair yield. The diphenyl and bis-(4-chlorophenyl) cases **2d** and **2e**, respectively, led to a mixture of the rearrangement urazoles **3d** and **3e** and the double PTAD [4 + 2] cycloadducts **4d** and **4e** in form of the *syn/syn* and *syn/anti* diastereomers. Analogously, the unsymmetrically substituted 7-(diarylmethylene)benzonorbornadienes **2c** (X = Ph, Y = *p*-MeOPh) and **2f** (X = Ph, Y = *p*-NO_2Ph) gave similar products, except that the possible diastereomeric rearrangement urazoles were formed (*E,Z*-**3c** and *E,Z*-**3f**). In the case of **2c** the oxidized monocycloadduct **5c** was also isolated in low yield. The ratio of rearrangement urazoles **3** to [4 + 2] cycloaddition products **4** increased with increasing electron withdrawal of the substituents on the aryl groups, i.e. it was largest for *p*-nitrophenyl and smallest for *p*-methoxyphenyl. NOE studies and X-ray analyses (of **3b**, of **4d** with NMe instead of NPh, and of **5c**) were essential to assign the stereochemistry of these complex products.

Cycloaddition von 4-Phenyl-4*H*-1,2,4-triazol-3,5-dion (PTAD) an 7-Alkyliden-2,3-benzonorbornadiene

Die Umsetzung einer Reihe von Fulvenen **1a–f** mit Dehydrobenzol führte zu den entsprechenden 7-Alkyliden-2,3-benzonorbornadienen **2a–f**, deren Cycloadditionen mit PTAD untersucht wurden. Während das Phenyl-Derivat **2a** kaum reagierte und nur Spuren des [2 + 2]-Cycloaddukts **3a** lieferte, ergab das Phenylmethyl-System **2b** das En-Produkt **3b** in ansprechender Ausbeute. Im Falle der 6,6-Diphenyl- und 6,6-Bis(4-chlorphenyl)fulvene **2d** und **2e** wurden die Umlagerungs-Urazole **3d** und **3e** sowie die *syn/syn*- und *syn/anti*-Diastereomere **4d** und **4e** erhalten, die aus sukzessiven [4 + 2]-Cycloadditionen zweier Äquivalente PTAD resultierten. Die unsymmetrisch substituierten 7-(Diarylmethylen)benzonorbornadiene **2c** (X = Ph, Y = *p*-MeOPh) und **2f** (X = Ph, Y = *p*-NO_2Ph) führten zu analogen Produkten, wobei die Umlagerungs-Urazole als Diastereomerenpaare *E/Z*-**3c** und *E/Z*-**3f** erhalten wurden. Im Falle von **2c** konnte auch das oxidierte Monoaddukt **5c** in geringer Ausbeute isoliert werden. Das Verhältnis der aus Umlagerung zu den aus [4 + 2]-Cycloadditionen resultierenden Urazolen steigt mit zunehmendem elektronenziehendem Charakter der Substituenten am Arylrest, d. h. es ist am höchsten für Y = *p*-NO_2Ph und am niedrigsten für Y = *p*-MeOPh. NOE-Untersuchungen und Röntgenstrukturanalysen (von **3b**, von **4d** mit NMe statt NPh und von **5c**) waren zur Bestimmung der Stereochemie dieser komplexen Produkte nötig.

For our mechanistic studies on the thermal and photochemical denitrogenation of azoalkanes[1] we required a series of 5-alkylidene-substituted 2,3-diaza-7,8-benzotricyclo-[4.3.0.$0^{4,9}$]non-7-enes, potentially available by the synthetic route shown in eq. (1)[2]. In view of the propensity of 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) to engage in diverse cycloaddition modes[3] besides the desired urazoles, derived from such dipolar rearrangements (eq. 1), [2 + 2] cycloaddition of PTAD at the exo- and endocyclic double bonds were expected. Moreover, for methyl substituents at the 7-alkylidene double bond ene products were likely, while for phenyl substituents [4 + 2] cycloadducts were probable



(1)

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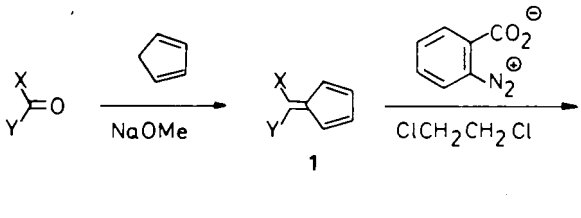
in which the phenyl moiety becomes part of the required 1,3-diene system. Since especially aryl-substituted azoalkanes (eq. 1) were of interest, it was essential to explore whether the desired cycloaddition mode, i.e. dipolar rearrangement, of PTAD with 7-alkylidene-2,3-benzonorbornadienes would predominate among the numerous alternatives. Herein we report the results of this study.

Preparation of 7-Alkylidene-2,3-benzonorbornadienes 2

The synthesis of **2** was carried out according to eq. (2). The fulvenes **1**, all known compounds, were prepared by means of Knoevenagel condensation of the respective carbonyl component with cyclopentadiene. Subsequent addition of benzyne, made available from diazotization of anthranilic acid, to the fulvenes **1** afforded the required 7-alkylidene-2,3-benzonorbornadienes **2**. Of these only the diphenyl derivative **2d**[2] was known.



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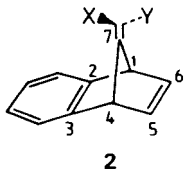
(2)



2

	X	Y
a	Ph	H
b	Ph	Me
c	Ph	4-$MeOC_6H_4$
d	Ph	Ph
e	4-ClC_6H_4	4-ClC_6H_4
f	Ph	4-$NO_2C_6H_4$

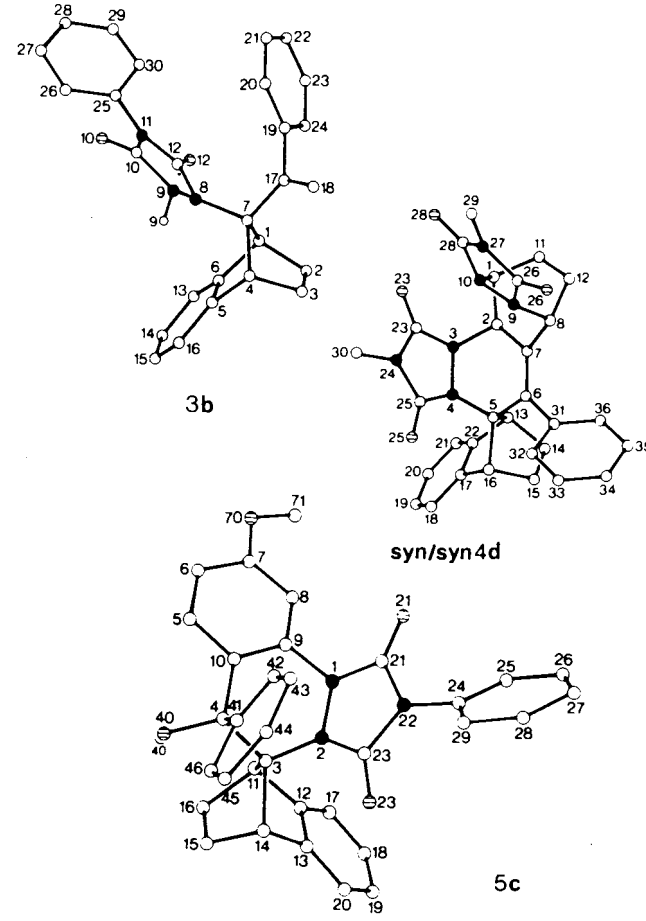
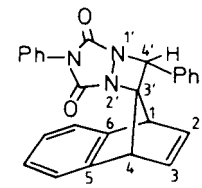


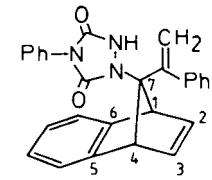
Figure 1. Perspective drawings of the structures **3b**, *syn/syn*-**4d** (NMc instead of NPh) and **5c**; the open, solid, and hatched circles represent carbon, nitrogen, and oxygen atoms, respectively, and their numbering refers to that of Tables 3–5

Product Studies of the Cycloaddition of PTAD with the 7-Alkylidene-2,3-benzonorbornadienes 2

As expected, the reaction with PTAD was complex, leading to diverse products derived from the various possible cycloaddition modes (Table 1). The benzonorbornadiene derivatives **2a** and **2b** are not listed, because their cycloaddi-



3a



3b

Table 1. Product data of the cycloaddition of PTAD to 7-alkylidene-2,3-benzonorbornadiene **2** in dichloromethane

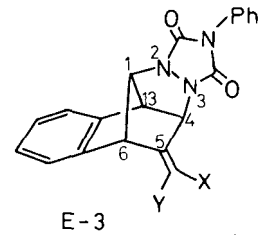
No.	Conversion [%]	Mass Balance [%][a]	Absolute Yields [%][c]				Relative Yields [%][d]	
			E-**3**	*Z*-**3**	*syn/syn*-**4**	*syn/anti*-**4**	**3**	**4**
2c	100	34	2/3[b]		27[e] (2[f])		15	85
2d	53	99	29[g]		10	13	56	44
2e	100	46	36[g]		6	4	78	22
2f	100	51	24	17	5	7	77	23

[a] Remainder was undefined high-molecular-weight products that were retained on the silica gel column. – [b] *E,Z* stereochemistry not defined. – [c] Isolated yields after silica gel chromatography, error ca. 10% of stated value. – [d] Normalized to 100%. – [e] The available spectral data did not permit determining whether the cycloadduct has *syn/anti* or *syn/syn* configuration, but only one of them is formed. – [f] This minor product is the [4 + 2] rearranged monocycloadduct **5c** as confirmed by X-ray analysis. – [g] No *E,Z* diastereomers possible.

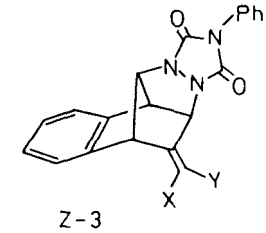
tion behavior towards PTAD was distinct from that of the diaryl derivatives **2c–f**. For example, in the case of **2a** only ca. 0.5% of the [2 + 2] cycloadduct **3a** could be isolated. On the other hand, **2b** gave as expected only the ene product **3b** in 46% yield. Its structure was confirmed by means of X-ray analysis (cf. Figure 1). The mass balance, except for the parent system **2d**, was rather low (Table 1), which is quite typical for relatively sluggish PTAD cycloadditions. Substantial amounts of insoluble and undefined material was formed which was retained on the chromatography column.

The [2 + 2] cycloaddition mode at the 7-alkylidene double bond is of no importance, since the major products are the rearrangement urazoles *E*/*Z*-**3** and the double [4 + 2] cycloaddition urazoles *syn/syn*- and *syn/anti*-**4**. The sum of rearrangement products **3** versus the sum of double [4 + 2] cycloaddition products **4** exhibit a clear substituent effect (Table 1) for the derivatives **2c–f** investigated here. Thus, electron donors as in **2c** promote double [4 + 2] cycloaddition, while electron acceptors as in **2e,f** promote rearrangement. As expected, both the *E* and *Z* isomers of the rearrangement urazoles **3** are formed (Table 1), except of course for the benzonorbornadienes **2d** and **2e**. The small differences in the yields of the stereoisomers *E*,*Z*-**3f** should be not necessarily be construed as a directing effect by the nitro substituent on the rearrangement course[4].

More complex is the stereochemical course of the double [4 + 2] cycloaddition mode. For a symmetrically substituted derivative (X = Y), e.g. **2d** and **2e**, the four *syn/syn*, *syn/anti*, *anti/syn*, and *anti/anti* diurazoles **4** can be formed in principle. Here the benzo ring serves as reference point in defining the *anti/syn* stereochemistry of the diurazoles, for which the first *anti/syn* assignment refers to attack by PTAD at the C-7 double bond and the second to the attack on the resulting 1,3-cyclohexadiene moiety. Of these possibilities we have no evidence for cycloadducts with the *anti/syn* and *anti/anti* stereochemistry, i.e. attack of the first PTAD at the C-7 double bond, but from the side opposite to the benzo ring. Instead, PTAD first attacks exclusively from the benzo side, as confirmed by X-ray analysis of the cycloadduct *syn/*



E-3



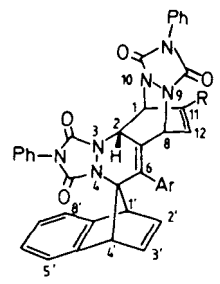
Z-3

	X	Y
3c	Ph	4-$MeOC_6H_4$
d	Ph	Ph
e	4-ClC_6H_4	4-ClC_6H_4
f	O_2N-	

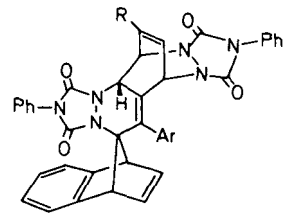
syn-**4d** (cf. Figure 1). In this case it was essential to use methyl (MTAD) in place of phenyl (PTAD) substituted triazoledione, because the latter cycloadduct was not suitable for X-ray analysis. Also the ene product **3b**, derived from PTAD and **2b**, was formed exclusively by *syn* attack, as established by X-ray analysis (cf. Figure 1). This is analogous to the 7-isopropylidenebenzonorbornadiene but contrary to the 7-isopropylidenebenzonorbornene[5], for which *anti* attack is preferred.

Another interesting feature in the addition of the first PTAD molecule is the regioselectivity observed for the unsymmetrical diaryl substrates **2c** (*p*-MeO) and **2f** (*p*-NO_2). The former undergoes exclusive [4 + 2] cycloaddition at the *p*-methoxyphenyl substituent, the latter not at the *p*-nitrophenyl group. This is in accord with the electrophilic nature of PTAD, a reagent which chooses electron-rich centers preferably. Stereochemical *anti/syn* differentiation during the cycloaddition of the second PTAD molecule is less pronounced than that of the first.

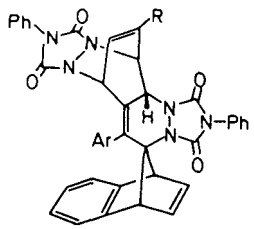
Obscure is the mechanistic origin of the monoadduct **5c** from the methoxy substrate **2c**. The structure assignment rests on an X-ray analysis (Figure 1). Clearly, the cycloadduct of the first PTAD addition is somehow oxidized, but on the actual course we can only speculate (eq. 3). The electron-rich triene moiety should be prone towards electron transfer with PTAD[6], and the corresponding radical cation after hydrogen atom transfer would generate the stabilized benzhydryl-type cation. Direct capture by water or hydrolysis during silica gel chromatography of the urazole, that is formed on collapse of the ions, would result in the oxidized



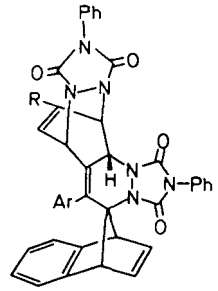
syn/syn-4



syn/anti-4

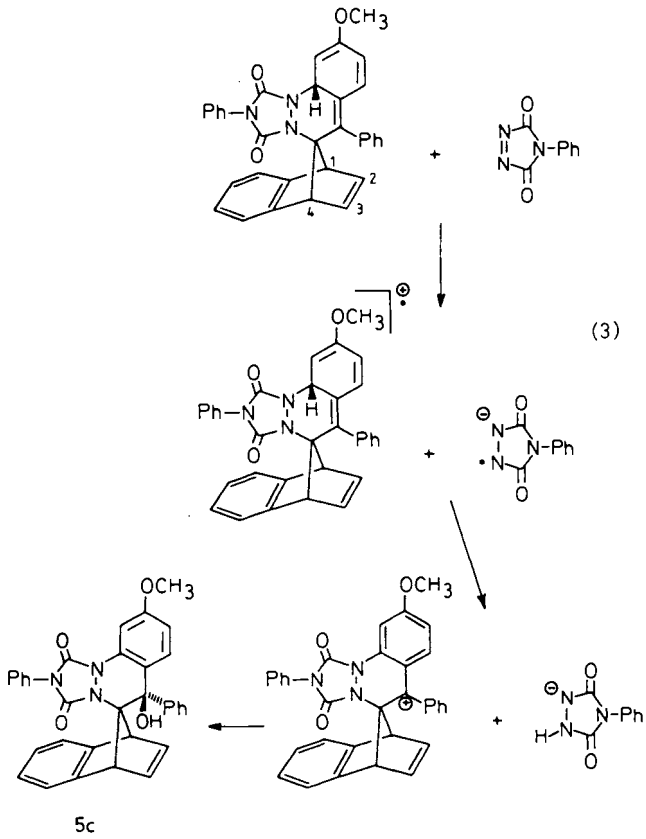


anti/syn-4



anti/anti-4

	Ar	R
4c	Ph	MeO
d	Ph	H
e	4-ClC_6H_4	Cl
f	4-$NO_2C_6H_4$	H



monoadduct **5c**. Other mechanisms are possible, but they must take into consideration the fact that only for the methoxy substrate **2c** oxidation competes with the cycloaddition of the second PTAD molecule.

Nuclear Overhauser Enhancement (NOE) Studies

Besides X-ray structure determinations of the cycloadducts **3b**, **5c**, and *syn/syn*-**4d** (NMe instead of NPh) (cf. Figure 1), also NOE studies were performed on **3a**, *E*-**3f**, *Z*-**3f**, *syn/syn*-**4d**, *syn/anti*-**4d**, and *syn/syn*-**4f**. These provided valuable insights into the stereochemistry of these complex products. The order of presentation follows the above sequence. Only the salient features, that were decisive in the structural assignment, are reproduced here.

[2 + 2] Cycloadduct 3a

The NOE experiments on **3a** were undertaken in $CDCl_3$. The uncoupled singlet at δ 5.46 belongs to proton 4′-H. When it was saturated, the bridgehead proton 1-H was identified as the broad singlet at δ 4.18 (8.0% enhancement) and the phenyl *ortho* protons at δ 7.52 (9.0% enhancement). In turn, irradiation of 1-H gave 12.6% enhancement of the olefinic proton 2-H at δ 6.63 and 4.0% enhancement of the proximate benzo *ortho* proton at δ 7.35, while the irradiation of the other bridgehead proton 4-H at δ 3.95 induced 11.1% enhancement of the 3-H olefinic proton at δ 6.18 and 4.8% enhancement of the proximate benzo *ortho* proton at δ 7.32. The saturation of the methinyl proton 4′-H resulted in 0.9 and 0.6% enhancements of the olefinic protons 2-H and 3-H, respectively, but none of the benzo protons. The same olefinic resonances were enhanced (1.4 and 1.7%, respectively) when the phenyl *ortho* protons were saturated. This definitely places the urazole ring on the benzo side of the benzonorbornadiene moiety.

Rearrangement Urazoles *E,Z*-3f

For both urazoles the two highest field multiplets are attributed to the bridgehead protons 6-H and 13-H at δ 4.21 and 3.88 for *E*-**3f** and δ 4.34 and 3.94 for *Z*-**3f**, respectively (from NOE experiments in $CDCl_3$).

The two lowest field nonaromatic resonances belong to the protons 1-H and 4-H vicinal to the urazole ring and resonate at δ 4.91 and 5.24 for *E*-**3f** and δ 4.88 and 5.16 for *Z*-**3f**. In the *E* (*Z*) isomer, irradiation of the high-field multiplet at δ 3.88 (3.94) led to 13.1 and 12.3% (12.3 and 11.9% enhancement) of both low-field resonances at δ 4.91 and 5.24 (4.88 and 5.16), while only the former was 16.6% (15.0%) enhanced when the other high-field resonance at δ 4.21 (4.34) was saturated. Reverse saturation experiments confirmed the assignments of the resonances at δ 5.24, 4.91, 4.21, and 3.88 (5.16, 4.88, 4.34, and 3.94) to 4-H, 1-H, 6-H, and 13-H, in that order.

In the *E*-**3f** isomer the saturation of the low-field proton 6-H caused 4.8 and −0.8% enhancement of the doublets at δ 7.29 and 8.27, respectively, which display the typical pattern for the protons 3′-H and 5′-H of the *para*-substituted phenyl ring. On the other hand, the multiplet at δ 7.09, which was 9.1 and −1.0% enhanced following saturation of 4-H and 13-H, respectively, was attributed to the *ortho* protons 2″-H and 6″-H of the unsubstituted phenyl group. Therefore, in the *E*-**3f** isomer the *para*-nitrophenyl and the phenyl groups are proximate to 6-H and 4-H, respectively.

In the *Z*-**3f** isomer the *ortho* and *meta* protons of the *para*-nitrophenyl group were 8.9 and −1.7%, respectively, enhanced when the high-field proton 4-H was irradiated. Saturation of the low-field proton 6-H caused 5.1% enhancement of the *ortho*-protons 2″-H and 6″-H of the unsubstituted phenyl ring at δ 7.06. This locates the *para*-nitrophenyl and phenyl rings in the *Z*-**3f** diastereomer proximate to the protons 4-H and 6-H, respectively.

[4 + 2] Cycloadducts *syn/syn*- and *syn/anti*-4d

The NOE measurements for these cycloadducts were performed in [D_6]benzene, where the signals are separated sufficiently for a reliable analysis. Inspection of molecular models revealed that the phenyl ring bound to olefinic carbon C-6 is rotationally hindered. Indeed, in the present NOE study two separate *ortho* resonances are observed.

In isomer *syn/syn*-**4d** (*syn/anti*-**4d**) the 2-H resonance was easily identified as a doublet at δ 4.14 (4.75), while the two other broad signals at δ 3.92 (4.14) and 4.75 (4.95) were attributed to the bridgehead protons 4′-H and 1′-H. Irradiation of the high-field resonance at δ 3.92 (4.14) brought about a 18.2% (24.9%) enhancement of the 2-H doublet. This permitted assigning the signal to 4′-H. The same experiment induced 11.4% (12.2%) enhancement of the olefinic 3′-H resonance at δ 6.04 (6.10) and 7.2% (7.8%) enhance-

ment of benzo proton 5'-H at δ 7.22 (7.28). Also negative −1.4% (−3.7%) enhancement of 1-H at δ 6.76 (6.58) was observed to be attributed to the fact that the protons 4'-H, 2-H, and 1-H are in a quasi colinear arrangement. On the other hand, on saturation of 1'-H at δ 4.75 (4.95) the resonance of the olefinic proton 2'-H at δ 5.68 (5.69) was identified on the basis of 11.1% (12.8%) enhancement and the benzo proton 8'-H at δ 7.50 (7.48) with 4.8% (9.0%) enhancement. More important, from this perturbational experiment one *ortho*-H resonance of the phenyl ring at the C-6 position was singled out in the differential mode from the otherwise untractable aromatic pattern at δ 7.38 (7.17) as the result of a 10.0% (6.5%) enhancement. Since some rotation around the C-6 phenyl bond still takes place, exchange-induced polarization transfer caused 2.1% (1.7%) enhancement of the other *ortho* proton, identified as a multiplet at δ 6.69 (7.07). These assignments were confirmed by irradiation of 8-H at δ 5.19 (5.39) which provoked 1.5 and 7.5% (1.0 and 2.1%) enhancement of the *ortho*-H resonances at δ 7.38 and 6.69 (7.17 and 7.07), respectively. Finally, on saturation of 1-H the olefinic proton 11-H at δ 5.85 (6.05) was identified with 7.7% (17.4%) enhancement.

This detailed assignment is a prerequisite for the configurational analysis which follows. When in the isomer *syn/syn*-**4d** (*syn/anti*-**4d**) the aromatic region around δ 6.69 (7.07) is irradiated, 2.6 and 1.3% (2.5 and 2.3%) enhancement of the olefinic protons 3'-H and 2'-H, respectively, were observed. This permits placing the 3,4-urazole ring above the benzo moiety in the benzonorbornadiene. Furthermore, in the *syn/syn*-**4d** isomer mutual positive enhancements are observed between methinyl proton 2-H and the olefinic proton 11-H (irradiation of 2-H enhanced the 11-H signal by 1.3%, the reverse experiment led to 2.2% enhancement of 2-H), implying that 2-H is *exo* to the second 9,10-urazole ring. The saturation of 2-H in the *syn/anti*-**4d** isomer induced a negative −1.9% enhancement of the 11-H resonance, due to the fact that the 2-H, 1-H, and 11-H protons are almost colinear when 2-H is *endo* to the second urazole ring. The complimentary experiment is not significant, as the irradiation of the proton 11-H unavoidably saturates the almost isochronous proton 3'-H. The observed negative enhancement (−1.9%) of the 2-H signal in this experiment results from the colinearity of 2-H, 4'-H, and 3'-H.

[4 + 2] Cycloadduct *syn/syn*-4f

Also these saturation studies were conducted in [D_6]benzene. Thus, in the saturation of 4'-H at δ 3.86, 2-H at δ 4.10 (15.4% enhancement), 3'-H at δ 5.94 (11.5% enhancement), 5'-H at δ 7.20 (7.1% enhancement), and 1-H at δ 6.73 (−1.4% enhancement) were identified. The irradiation of 1'-H revealed 2'-H at δ 5.39 (10.6% enhancement), 8'-H at δ 7.54 (6.1% enhancement) and the two *ortho* proton resonances of the *para*-nitrophenyl ring at δ 7.10 (9.8% enhancement) and δ 6.29 (1.4% enhancement). These two latter assignments were confirmed by saturation of 8-H at δ 4.96, with 1.1 and 6.8% enhancements, respectively. The perturbation of 1-H induced 6.0% enhancement of 11-H, isochronous with 12-H.

The irradiation of the *ortho*-H multiplet at δ 6.29 induced 2.2 and 1.0% enhancements of the 3'-H and 2'-H olefinic resonances, respectively. Thus, the benzo ring in this benzonorbornadiene is located under the 3,4-urazole ring. From the saturation of 2-H the resonance of the 11-H proton is enhanced by 1.0% while the reverse experiment caused a 1.7% enhancement of the 2-H proton. The comparison of the results with those obtained for the *syn/syn* and *syn/anti* pair of **4d** confirmed that the 2-H proton is *exo* to the 9,10-urazole ring.

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Experimental

Infrared spectra: Perkin Elmer Infrared Spectrophotometer 1420 and Beckman Acculab 4. – ^{1}H-NMR spectra: Hitachi-Perkin-Elmer R-24 B (60 MHz), Varian EM-390 (90 MHz), Bruker AC 200 (200 MHz), or Bruker WM-400 (400 MHz). – ^{13}C-NMR spectra: Bruker AC 200 (50 MHz) or Bruker WM 400 (100 MHz). Chemical shifts are given in δ values relative to tetramethylsilane for protons and deuteriochloroform for carbon atoms. – Mass spectra (MS): Varian MAT CH 7. – Melting points: Reichert Thermovar Kofler apparatus, uncorrected. – Combustion analyses: Either in-house or by Prof. *G. Maier*'s staff at the Institut für Organische Chemie, Universität Gießen. – Thin layer chromatography (TLC): Polygram SIL/G/UV (40 × 80 mm), Machery & Nagel Co. – All

Table 2. X-ray operations and results of the cycloadducts **3b**, *syn/syn*-**4d** (NMe instead of NPh), and **5c**

Crystallographic section			
empirical formula	$C_{27}H_{21}N_3O_2$	$C_{30}H_{24}N_6O_4$	$C_{33}H_{28}N_3O_4$
molecular mass	419.48	532.56	527.58
a [pm]	2809.2(18)	1285.1(2)	1756.2(4)
b [pm]	789.8(4)	2596.6(3)	1277.7(4)
c [pm]	2097.4(12)	880.0(2)	1157.0(3)
β [pm]	113.39(4)	104.78(1)	92.43(2)
V [$pm^3 \cdot 10^{-6}$]	4271(9)	2838.1(7)	2594(1)
Z	8	4	4
d(calcd) [$g \cdot cm^{-3}$]	1.305	1.246	1.351
crystal system		monoclinic	
space group	C2/c	$P2_1/n$	$P2_1/n$
Data collection			
diffractometer		Syntex P3	
radiation		MoKα	
monochromator		graphite	
crystal size [mm]	1.0x1.1x0.15	0.4x1.2x0.2	0.65x0.7x0.35
data collection mode		ω-scan	
theta range [deg]		1.75 - 27.5	
recip. latt. segment	h = 0 - 36 k = 0 - 10 l = -29 - 25	h = 0 - 16 k = 0 - 33 l = -11 - 11	h = 0 - 22 k = 0 - 16 l = -15 - 15
no. refl. measd.	3990	5437	5950
no. unique refl.	3772	5106	5595
no. refl. F>3σ(F)	3305	4059	5171
lin. abs. coeff. [cm^{-1}]	0.78	0.87	0.84
abs. correction		ψ-scan	
Structural analysis and refinement			
solution by	direct phase determination		
method of refinement	anisotropic block diagonal matrix least sqares; hydrogen positions were calculated and considered isotropically		
parameter/Fo ratio	0.088	0.096	0.070
R, Rw	0.060, 0.056	0.062, 0.058	0.053, 0.054
program used		SHELXTL	

known compounds used were either purchased or prepared according to reported methods and purified to match the reported physical and spectral data. Unless otherwise stated, rotoevaporation of the solvent was carried out at ca. 20–25°C/10–20 Torr (water aspirator) and drying was carried out with sodium sulfate. – Column chromatography (CC): silica gel (32–63 μm), substrate to adsorbant ratio ca. 1:20, column length to width dimensions ca. 16:1. – Room temperature refers to ca. 20°C.

Crystallographic Work[7] *on the Cycloadducts* **3b**, **5c**, *and syn/syn-*4**d** (NMe instead of NPh): The operations and results are summarized in Table 2, the positional and thermal parameters in Tables 3–5, and the structures exhibited in Figure 1. Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. These data are available with quotation of the registry number CSD-53217, the authors, and the reference to this publication.

Table 3. Positional ($\times 10^4$) and thermal ($pm^2 \times 10^{-1}$) parameters for the atoms of the cycloadduct **3b**. The numbering of the atoms is given in Figure 1 (standard deviations in parentheses)

	x	y	z	U_{EQ}
C(1)	3022(1)	3643(4)	-341(1)	52(1)
C(2)	2647(1)	5136(4)	-435(2)	62(1)
C(3)	2879(1)	6519(4)	-526(2)	67(1)
C(4)	3413(1)	6021(4)	-504(2)	60(1)
C(5)	3301(1)	4917(4)	-1144(2)	62(1)
C(6)	3062(1)	3433(4)	-1049(1)	58(1)
C(7)	3547(1)	4610(4)	72(1)	48(1)
N(8)	3993(1)	3576(3)	100(1)	47(1)
N(9)	4468(1)	4450(3)	293(1)	50(1)
C(10)	4862(1)	3293(4)	554(1)	47(1)
O(10)	5322(1)	3541(3)	688(1)	58(1)
N(11)	4636(1)	1787(3)	630(1)	46(1)
C(12)	4096(1)	1928(4)	342(1)	46(1)
O(12)	3783(1)	829(2)	296(1)	58(1)
C(13)	2896(1)	2183(5)	-1546(2)	74(1)
C(14)	2959(1)	2449(6)	-2172(2)	91(2)
C(15)	3192(1)	3912(6)	-2267(2)	96(2)
C(16)	3372(1)	5166(5)	-1755(2)	81(2)
C(17)	3643(1)	5233(4)	799(1)	50(1)
C(18)	3678(1)	6843(4)	980(2)	70(1)
C(19)	3731(1)	3888(4)	1345(1)	49(1)
C(20)	4219(1)	3640(4)	1863(2)	65(1)
C(21)	4297(1)	2413(5)	2372(2)	76(1)
C(22)	3899(1)	1429(4)	2364(2)	72(1)
C(23)	3408(1)	1670(4)	1861(2)	75(1)
C(24)	3326(1)	2902(4)	1353(1)	65(1)
C(25)	4918(1)	256(3)	936(1)	47(1)
C(26)	5361(1)	-181(4)	840(1)	54(1)
C(27)	5621(1)	-1660(4)	1142(1)	64(1)
C(28)	5441(1)	-2678(4)	1531(2)	70(1)
C(29)	5003(1)	-2226(4)	1623(2)	69(1)
C(30)	4737(1)	-733(4)	1341(1)	56(1)

Nuclear Overhauser Spectroscopy of the Cycloadducts **3a**, *E-*3**f**, *Z-*3**f**, *syn/syn-*4**d**, *syn/anti-*4**d**, *and syn/syn-*4**f**: The NOE experiments were carried out with a Bruker WP 200 SY instrument. The sample (in $CDCl_3$ or C_6D_6) was freed from oxygen by sonication under N_2 gas purging. The usual procedure for gated irradiation experiments was modified[8], and the selected resonance was saturated by an 8-s cyclic perturbation of all lines with a 38–40 dB attenuation of a nominal 0.2-W decoupling power. The enhancements (in %) were obtained from the multiplier of the reference spectrum by bringing the observed multiplet to exact matching with the corresponding multiplet in the perturbed spectrum. Errors are ca. 0.3%. By careful choice of the multiplier in most cases it was possible in the differential mode to single out a pure multiplet from a bunch of overlapping signals.

Table 4. Positional ($\times 10^4$) and thermal ($pm^2 \times 10^{-1}$) parameters for the atoms of the cycloadduct *syn/syn-*4**d** (NMe instead of NPh). The numbering of the atoms is given in Figure 1 (standard deviations in parentheses)

	x	y	z	U_{EQ}
C(1)	6816(2)	-267(1)	5820(4)	55(1)
C(2)	6508(2)	293(1)	5308(3)	48(1)
N(3)	5909(2)	578(1)	6325(3)	49(1)
N(4)	6261(2)	1102(1)	6697(3)	49(1)
C(5)	6663(2)	1372(1)	5504(3)	48(1)
C(6)	7659(2)	1077(1)	5344(3)	45(1)
C(7)	7556(2)	568(1)	5272(3)	44(1)
C(8)	8480(2)	188(1)	5442(3)	52(1)
N(9)	8643(2)	5(1)	7078(3)	52(1)
N(10)	7686(2)	-234(1)	7305(3)	55(1)
C(11)	7265(3)	-503(1)	4573(4)	65(1)
C(12)	8122(3)	-269(1)	4352(4)	62(1)
C(13)	5768(2)	1434(1)	3909(3)	52(1)
C(14)	6409(3)	1791(1)	3094(4)	61(1)
C(15)	6987(3)	2103(1)	4170(4)	62(1)
C(16)	6771(2)	1967(1)	5754(4)	56(1)
C(17)	5595(3)	2110(1)	5586(4)	58(1)
C(18)	5134(3)	2506(1)	6228(4)	72(1)
C(19)	4024(3)	2573(1)	5711(5)	82(2)
C(20)	3409(3)	2253(1)	4592(4)	74(1)
C(21)	3867(3)	1847(1)	3938(4)	64(1)
C(22)	4970(2)	1785(1)	4450(3)	55(1)
C(23)	5906(2)	350(1)	7788(3)	53(1)
O(23)	5537(2)	-67(1)	7962(2)	68(1)
N(24)	6362(2)	698(1)	8927(3)	58(1)
C(25)	6645(2)	1152(1)	8297(3)	54(1)
O(25)	7084(2)	1524(1)	9023(2)	74(1)
C(26)	9529(3)	-271(1)	7898(4)	60(1)
O(26)	10463(2)	-190(1)	7936(3)	77(1)
N(27)	9117(2)	-637(1)	8729(3)	65(1)
C(28)	8007(3)	-653(1)	8289(4)	66(1)
O(28)	7426(2)	-961(1)	8712(3)	89(1)
C(29)	9789(3)	-969(1)	9951(4)	90(2)
C(30)	6540(3)	596(1)	10601(4)	85(2)
C(31)	8706(2)	1341(1)	5477(3)	47(1)
C(32)	9181(2)	1631(1)	6802(3)	55(1)
C(33)	10170(3)	1868(1)	6945(4)	72(1)
C(34)	10698(3)	1811(1)	5771(4)	80(1)
C(35)	10248(3)	1524(1)	4453(4)	72(1)
C(36)	9251(3)	1291(1)	4287(4)	59(1)
O(37)	3987(4)	1009(2)	9139(6)	211(3)
C(38)	3613(8)	1507(3)	8545(7)	205(5)
C(39)	4205(6)	1858(3)	9534(7)	175(4)

General Procedure for the Preparation of 2,3-Benzobicyclo[2.2.1]-hepta-2,5-dienes (Tricyclo[6.2.1.0^{2,7}*]undeca-2,4,6,9-tetraenes)* **2a**–**f**: A solution of 50.0 mmol of anthranilic acid in 15 ml of diglyme was added dropwise over a period of 1 h to a solution of 30.0 mmol of the corresponding fulvene and of 50.0 mmol of isoamyl nitrite in ca. 100 ml of ethylene chloride, maintaining gentle reflux. The reaction mixture was refluxed for an additional 1 h. The mixture was allowed to cool to room temp. and was washed with 10 ml of 1 M potassium carbonate solution and 100 ml of water (2 × 50 ml). After drying of the organic layer and removal of the solvent, the crude product was purified by flash CC, eluting with a gradient of petroleum ether (30–75°C/methylene chloride.

Benzylidene Derivative **2a**: 8.00 g (21%) of **2a** was obtained as a colorless oil, b. p. 150–160°C at 20 Torr, starting from 26.0 g (169 mmol) of 6-phenylfulvene. – IR (film): $\tilde{\nu}$ = 3065 cm^{-1}, 3022, 2925, 1688, 1605, 1598, 1497, 1450, 810, 785, 751, 702, 675. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.24 (m, 1H, 1-H), 4.74 (m, 1H, 4-H), 5.38 (s, 1H, C*H*Ph), 6.92–7.30 (m, 11H, aromatic H, 5-, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 50.2 (d), 54.8 (d), 102.3 (d), 121.2 (d),

121.4 (d), 124.9 (d), 125.1 (d), 126.1 (d), 128.1 (d), 128.3 (d), 136.8 (s), 142.4 (d), 142.8 (d), 149.0 (s), 149.5 (s), 167.3 (s). – MS (70 eV): *m/z* (%) = 231 (15) [M + 1], 230 (90) [M$^+$], 229 (100) [M – 1], 228 (44), 227 (16), 226 (16), 215 (25), 203 (10) [M – 28], 202 (20), 152 (9), 128 (18), 115 (26), 114 (10), 101 (14).

$C_{18}H_{14}$ (230.3) Calcd. C 93.87 H 6.13
Found C 93.96 H 5.95

Table 5. Positional ($\times 10^4$) and thermal ($pm^2 \times 10^{-1}$) parameters for the atoms of the cycloadduct **5c**. The numbering of the atoms is given in Figure 1 (standard deviations in parentheses)

	x	y	z	U_{EQ}
N(1)	2705(1)	7843(1)	8336(1)	34(1)
N(2)	2460(1)	8122(1)	9451(1)	33(1)
C(3)	2122(1)	9161(1)	9588(2)	35(1)
C(4)	2787(1)	9939(2)	9302(2)	38(1)
C(5)	3252(1)	10471(2)	7326(2)	39(1)
C(6)	3379(1)	10275(2)	6179(2)	41(1)
C(7)	3231(1)	9284(2)	5720(2)	39(1)
C(8)	2999(1)	8476(2)	6430(2)	37(1)
C(9)	2911(1)	8690(1)	7596(1)	33(1)
C(10)	2999(1)	9691(2)	8063(2)	34(1)
C(11)	1346(1)	9265(2)	8849(2)	41(1)
C(12)	902(1)	8373(2)	9377(2)	42(1)
C(13)	1118(1)	8362(2)	10559(2)	41(1)
C(14)	1702(1)	9239(2)	10758(2)	41(1)
C(15)	1252(1)	10250(2)	10511(2)	51(1)
C(16)	1036(1)	10260(2)	9407(2)	51(1)
C(17)	365(1)	7695(2)	8924(2)	52(1)
C(18)	21(1)	7003(2)	9676(2)	60(1)
C(19)	226(1)	6996(2)	10836(2)	59(1)
C(20)	789(1)	7670(2)	11298(2)	50(1)
C(21)	3185(1)	6980(1)	8477(2)	36(1)
O(21)	3529(1)	6554(1)	7719(1)	49(1)
N(22)	3185(1)	6724(1)	9636(1)	35(1)
C(23)	2767(1)	7457(2)	10267(2)	35(1)
O(23)	2687(1)	7451(1)	11297(1)	46(1)
C(24)	3609(1)	5867(2)	10143(2)	39(1)
C(25)	3590(1)	4909(2)	9591(2)	48(1)
C(26)	4022(2)	4087(2)	10062(2)	64(1)
C(27)	4467(2)	4228(2)	11055(2)	70(1)
C(28)	4473(2)	5190(3)	11602(2)	69(1)
C(29)	4045(1)	6026(2)	11152(2)	53(1)
O(40)	2580(1)	11018(1)	9359(1)	50(1)
C(41)	3445(1)	9782(2)	10184(2)	46(1)
C(42)	4065(1)	9160(2)	9959(2)	54(1)
C(43)	4644(2)	8995(2)	10801(3)	76(1)
C(44)	4598(2)	9459(3)	11875(3)	91(1)
C(45)	3979(2)	10093(3)	12104(2)	89(1)
C(46)	3407(2)	10260(2)	11266(2)	67(1)
O(70)	3309(1)	9178(1)	4553(1)	50(1)
C(71)	3022(2)	8246(2)	4011(2)	60(1)

1-Phenylethylidene Derivative **2b**: 5.20 g (10%) of **2b** was obtained as colorless prisms, m.p. 81–82°C (hexane), starting from 36.0 g (214 mmol) of 6-methyl-6-phenylfulvene. – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1}, 3015, 2920, 1694, 1598, 1562, 1492, 1450, 1440, 1378, 1300, 1210, 815, 780, 768, 758, 710, 702, 690. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.92 (s, 3H, CH_3), 4.33 (m, 1H, 1-H), 4.50 (m, 1H, 4-H), 6.89–7.32 (m, 11H, aromatic H, 5-, 6-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.4 (q), 51.2 (d), 51.6 (d), 107.8 (s), 121.0 (d), 121.1 (d), 124.7 (d), 124.7 (d), 126.2 (s), 127.9 (d), 128.0 (d), 142.6 (d), 143.0 (d), 149.9 (s), 150.0 (s), 163.3 (s). – MS (70 eV): *m/z* (%) = 245 (11) [M + 1], 244 (53) [M$^+$], 229 (100), 228 (42), 227 (11), 226 (11), 215 (12), 202 (13), 129 (21), 128 (26), 115 (22), 114 (11).

$C_{19}H_{16}$ (244.3) Calcd. C 93.40 H 6.59
Found C 93.24 H 6.61

(4-Methoxyphenyl)phenylmethylene Derivative **2c**: 1.72 g (51%) of **2c** was obtained as an amorphous yellow solid, m.p. 43–45°C (petroleum ether 30–75°C), starting from 2.60 g (10.0 mmol) of 6-(4-methoxyphenyl)-6-phenylfulvene. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3018, 2960, 2940, 2840, 1608, 1510, 1452, 1441, 1245, 1178, 1032, 830, 760, 745, 710, 692. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.77 (s, 3H, OCH_3), 4.43 (m, 2H, 1-, 4-H), 6.82 (m, 2H, 5-, 6-H), 6.95–7.35 (m, 13H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.4 (d), 55.2 (q), 113.5 (d), 114.7 (s), 121.3 (d), 125.0 (d), 126.5 (d), 127.9 (d), 128.4 (d), 129.8 (d), 130.9 (d), 132.9 (s), 140.7 (s), 142.86 (d), 142.94 (d), 149.8 (s), 158.5 (s), 164.0 (s). – MS (70 eV): *m/z* (%) = 336 (0.3) [M$^+$], 305 (0.1), 195 (1), 112 (2), 105 (1), 92 (1), 91 (1), 78 (100), 77 (21).

$C_{25}H_{20}O$ (336.4) Calcd. C 89.25 H 5.99
Found C 89.43 H 6.13

Diphenylmethylene Derivative **2d**[2]: 3.74 g (19%) of **2d** was obtained as colorless needles, m.p. 131–132°C (pentane) (ref.[2] 131.5 to 132.5°C), starting from 15.0 g (65.1 mmol) of 6,6-diphenylfulvene. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ = 4.30 (m, 2H, 1-, 4-H), 6.70–7.30 (m, 16H, aromatic H, 5-, 6-H).

Bis(4-chlorophenyl)methylene Derivative **2e**: 7.30 g (73%) of **2e** was obtained as a colorless amorphous solid, m.p. 59–62°C (ethanol), starting from 8.00 g (26.7 mmol) of 6,6-bis(4-chlorophenyl)fulvene. – IR (CCl_4): $\tilde{\nu}$ = 3090 cm^{-1}, 3018, 2940, 1670, 1598, 1492, 1455, 1401, 1315, 1095, 1015, 837, 700, 688. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.39 (m, 2H, 1-, 4-H), 6.99 (m, 8H, 5-, 6-H, aromatic H), 7.25 (m, 6H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.2 (d), 113.0 (s), 121.4 (d), 125.3 (d), 128.3 (d), 131.0 (d), 132.7 (s), 138.4 (s), 142.7 (d), 149.0 (s), 164.8 (s). – MS (70 eV): *m/z* (%) = 378 (5) [M + 4], 377 (8) [M + 3], 376 (30) [M + 2], 374 (46) [M$^+$], 341 (25), 340 (24), 339 (71) [M – Cl], 305 (23), 304 (100) [M – 2Cl], 303 (73), 302 (45), 276 (18), 263 (18), 228 (34), 151 (37), 150 (24), 138 (26), 128 (39).

$C_{24}H_{16}Cl_2$ (375.3) Calcd. C 76.81 H 4.30
Found C 77.12 H 4.23

(4-Nitrophenyl)phenylmethylene Derivative **2f**: 1.38 g (52%) of **2f** was obtained as yellow needles, m.p. 184–185°C (petroleum ether 30–75°C), starting from 2.07 g (7.52 mmol) of 6-(4-nitrophenyl)-6-phenylfulvene. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 1650, 1595, 1513, 1445, 1340, 1278, 1105, 865, 850, 840, 770, 760, 750, 715, 695. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.41 (m, 1H), 4.46 (m, 1H), 7.00–7.35 (m, 13H, aromatic H, 5-, 6-H), 8.15 (m, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.1 (d), 52.3 (d), 121.4 (d), 121.6 (d), 123.4 (d), 125.4 (d), 125.5 (d), 127.3 (d), 128.4 (d), 129.8 (d), 130.4 (d), 139.4 (s), 142.5 (d), 142.8 (d), 148.7 (s), 148.8 (s), 166.0 (s). – MS (70 eV): *m/z* (%) = 352 (26) [M + 1], 351 (100) [M$^+$], 350 (25), 305 (24) [M – NO_2], 304 (38), 303 (43), 302 (32), 289 (24), 276 (20), 229 (81), 228 (35), 128 (43).

$C_{24}H_{17}NO_2$ (351.4) Calcd. C 82.03 H 4.88 N 3.99
Found C 82.34 H 4.83 N 3.92

General Procedure for the Reaction of Benzonorbornadienes **2a–f** *with 4-Phenyl-4H-1,2,4-triazole-3,5-dione* (PTAD): 10.0 mmol of PTAD was added in small portions to a solution of 5.00 mmol of the corresponding substituted benzonorbornadiene in 100 ml of dichloromethane, protected from light. The reaction was monitored by TLC at regular intervals. After complete turnover (from 24 h to 5 d) the reaction mixture was filtered to remove insoluble precipitates. The solvent was evaporated and the residue chromatographed on silica gel eluting, unless otherwise stated, with a gradient of petroleum ether (30–70°C)/dichloromethane.

[2 + 2]-Cycloadduct **3a**: The reaction of 3.80 g (16.5 mmol) of **2a** with 3.10 g (17.7 mmol) of PTAD at room temp. for 24 h yielded

36 mg (0.5%) of **3a** as colorless needles, m.p. 224–226°C (acetone). – IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1}, 3000, 1773, 1729, 1497, 1452, 1398, 1362, 1285, 1240, 1131, 1035, 1019, 790, 780, 768, 741, 640. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.95 (br. s, 1H, 4-H), 4.18 (br. s, 1H, 1-H), 5.46 (s, 1H, 4′-H), 6.18 (ddd, $J_{2,3}$ = 5.8, $J_{3,4}$ = 3.3, $J_{1,3}$ = 0.9 Hz, 1H, 3-H), 6.63 (ddd, $J_{2,3}$ = 5.8, $J_{1,2}$ = 3.3, $J_{2,4}$ = 0.9 Hz, 1H, 2-H), 7.12 (m, 2H, aromatic H), 7.31–7.54 (m, 12H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 54.3 (d), 54.6 (d), 71.9 (d), 102.0 (s), 123.4 (d), 123.5 (d), 125.2 (d), 126.1 (d), 126.3 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.0 (d), 129.1 (d), 135.8 (d), 135.0 (s), 141.4 (d), 142.8 (s), 146.4 (s), 158.5 (s). – MS (70 eV): *m/z* (%) = 406 (13) [M + 1], 405 (44) [M^+], 244 (18), 230 (43), 229 (100), 228 (68), 215 (20), 128 (45), 115 (27).

$C_{26}H_{19}N_3O_2$ (405.5) Calcd. C 77.02 H 4.72 N 10.36
Found C 77.15 H 4.72 N 10.51

Ene Product **3b**: From the reaction mixture of 1.37 g (5.61 mmol) of **2b** with 1.00 g (5.71 mmol) of PTAD at room temp. for 24 h 1.07 g (46%) of **3b** was isolated as colorless prisms, m.p. 199–200°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1}, 3150, 3060, 1762, 1700, 1601, 1496, 1415, 1300, 1262, 1232, 1137, 940, 781, 758, 749, 701, 630. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.58 (m, 2H, 1-, 4-H), 5.29 (s, 1H, vinyl-H), 5.56 (s, 1H, vinyl-H), 6.61 (dd, $J_{1,2}$ = $J_{2,4}$ = 2.2 Hz, 2H, 2-, 3-H), 6.94 (dd, *J* = 5.2; 3.1 Hz, 2H, Benzo-H), 7.22 (dd, *J* = 5.2; 3.1 Hz, 2H, Benzo-H), 7.26–7.50 (m, 10H, aromatic H), 9.37 (br. s, 1H, NH). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 56.5 (d), 97.9 (s), 120.2 (t), 123.1 (d), 125.4 (d), 125.6 (d), 127.6 (d), 128.1 (d), 128.9 (d), 131.1 (s), 140.3 (d), 141.1 (s), 147.0 (s), 147.7 (s), 150.6 (s), 153.4 (s). – MS (70 eV): *m/z* (%) = 419 (12) [M^+], 244 (22), 243 (100), 228 (17), 165 (13), 128 (22), 119 (23), 115 (27), 91 (22).

$C_{27}H_{21}N_3O_2$ (419.5) Calcd. C 77.31 H 5.05 N 10.02
Found C 77.27 H 5.05 N 9.94

The X-ray results are given in Tables 2 and 3 and the structure is exhibited in Figure 1.

Cycloaddition of PTAD to **2c**: From the reaction mixture of 2.25 g (6.69 mmol) of **2c** with 2.93 g (16.7 mmol) of PTAD in dichloromethane at 42°C for 3 d 100 mg (3%) of the cycloadduct **3c** (*E* or *Z*) was obtained as the first eluate as colorless prisms, m.p. 207–209°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2925, 2840, 1770, 1720, 1603, 1508, 1400, 1242, 1040, 780, 758, 745, 690. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.84 (s, 3H, OCH_3), 3.89 (m, 1H, 13-H), 4.35 (m, 1H, 6-H), 4.84 (m, 1H, 1-H), 5.20 (m, 1H, 4-H), 6.87–7.57 (m, 18H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.7 (d), 54.3 (d), 55.3 (q), 63.1 (d), 113.9 (d), 121.2 (d), 123.9 (d), 125.4 (d), 127.3 (d), 127.6 (d), 128.2 (d), 128.3 (d), 128.4 (d), 129.3 (d), 130.3 (d), 131.8 (s), 133.2 (s), 133.5 (s), 136.3 (s), 139.7 (s), 140.7 (s), 143.5 (s), 155.7 (s), 156.6 (s), 159.1 (s). – MS (70 eV): *m/z* (%) = 513 (15) [M + 1], 512 (43) [M^+], 336 (16), 335 (52), 334 (100), 333 (16), 323 (16), 303 (11), 291 (10), 221 (11), 215 (16), 119 (11).

$C_{33}H_{25}N_3O_3$ (511.6) Calcd. C 77.48 H 4.93 N 8.21
Found C 77.53 H 4.85 N 8.22

Next a fraction was obtained containing the cycloadducts **3c** (*Z* or *E*) and **5c**, which were separated by fractional crystallization from ethanol/acetone.

Cycloadduct **3c** (*Z* or *E*), 65 mg (2%), colorless prisms, m.p. 186–188°C (acetone). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3030, 2970, 2930, 1775, 1720, 1609, 1505, 1400, 1245, 1230, 1030, 760, 745, 708. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.76 (s, 3H, OCH_3), 3.88 (m, 1H, 13-H), 4.24 (m, 1H, 6-H), 4.84 (m, 1H, 1-H), 5.25 (m, 1H, 4-H), 6.85–7.56 (m, 18H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.7 (d), 54.3 (d), 55.2 (q), 62.9 (d), 113.6 (d), 121.3 (d), 123.9 (d), 125.4 (d), 127.2 (d), 127.5 (d), 128.2 (d), 128.4 (d), 129.1 (d), 129.3 (d), 130.5 (d), 131.6 (s), 132.8 (s), 132.9 (s), 136.2 (s), 139.3 (s), 141.0 (s), 143.4 (s), 155.7 (s), 156.6 (s), 159.0 (s). – MS (70 eV): *m/z* (%) = 512 (10) [M^+], 511 (36), 336 (13), 335 (50), 334 (100), 323 (17), 304 (11), 303 (16), 291 (15), 245 (11), 221 (12), 215 (31), 128 (19), 119 (35).

$C_{33}H_{25}N_3O_3$ (511.6) Calcd. C 77.48 H 4.93 N 8.21
Found C 77.23 H 4.78 N 8.16

Cycloadduct **5c**, 80 mg (2%), colorless prisms, m.p. 204°C (ethanol). – IR (CCl_4): $\tilde{\nu}$ = 3560 cm^{-1}, 3078, 2960, 2938, 1780, 1738, 1612, 1503, 1408, 1325, 1300, 1238, 1133, 1038, 910, 705. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.88 (s, 1H, OH), 3.92 (s, 3H, OCH_3), 3.99 (m, 1H), 4.79 (m, 1H), 6.97 (m, 7H, 2-, 3-H, aromatic H), 7.09–7.34 (m, 10H, aromatic H), 7.61 (m, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 53.5 (d), 55.6 (q), 56.7 (d), 79.0 (s), 96.4 (s), 101.7 (d), 112.3 (d), 122.2 (s), 122.4 (d), 124.0 (d), 124.9 (d), 125.2 (d), 125.7 (d), 126.7 (d), 128.1 (d), 128.2 (d), 128.8 (d), 130.8 (s), 134.3 (s), 139.4 (d), 141.4 (d), 142.9 (s), 145.6 (s), 147.1 (s), 148.9 (s), 150.0 (s), 160.1 (s). – MS (70 eV): *m/z* (%) = 528 (2) [M^+], 527 (6), 510 (15), 509 (39), 316 (14), 255 (13), 254 (69), 182 (43), 176 (51), 128 (100), 105 (44).

$C_{33}H_{25}N_3O_4$ (527.6) Calcd. C 75.13 H 4.78 N 7.96
Found C 75.38 H 4.82 N 7.89

The X-ray results are given in Tables 2 and 5, and the structure is exhibited in Figure 1.

As the fourth eluate, 1.25 g (27%) of cycloadduct **4c** was isolated in form of a colorless powder, m.p. 207–209°C (ethanol), whose *syn/syn* versus *syn/anti* configuration could not be assessed so far, but clearly it is one of these diastereomers. – IR (KBr): $\tilde{\nu}$ = 3015 cm^{-1}, 2960, 1788, 1765, 1712, 1632, 1508, 1412, 1250, 1228, 1135, 773, 745. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.50 (s, 3H, OCH_3), 4.44 (m, 1H, 4′-H), 4.61 (m, 1H, 1′-H), 5.09 (dd, $J_{8,12}$ = 7.0, $J_{1,12}$ = 2.8 Hz, 1H, 12-H), 5.21 (d, $J_{1,2}$ = 2.8 Hz, 1H, 2-H), 5.28 (d, $J_{8,12}$ = 7.0 Hz, 1H, 8-H), 6.08 (ddd, $J_{2',3'}$ = 5.5, $J_{1',2'}$ = 3.5, $J_{2',4'}$ = 0.9 Hz, 1H, 2′-H), 6.57 (dd, $J_{1,2}$ = $J_{1,12}$ = 2.8 Hz, 1H, 1-H), 6.61 (ddd, $J_{2',3'}$ = 5.5, $J_{3',4'}$ = 3.5, $J_{1',3'}$ = 0.9 Hz, 1H, 3′-H), 6.99–7.51 (m, 19H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 53.6 (d), 53.9 (d), 54.1 (q), 54.9 (d), 56.0 (d), 59.0 (d), 94.2 (s), 94.8 (d), 122.5 (d), 124.6 (d), 125.2 (d), 125.3 (d), 125.7 (d), 126.7 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.1 (d), 130.5 (s), 130.7 (d), 131.2 (s), 137.9 (s), 138.5 (d), 139.9 (s), 142.7 (d), 145.5 (s), 146.0 (s), 147.0 (s), 149.1 (s), 155.0 (s), 155.5 (s), 156.3 (s). – MS (70 eV): *m/z* (%) = 512 (1, M – PTAD), 511 (3), 383 (14), 336 (7), 249 (6), 177 (37), 129 (7), 128 (62), 120 (23), 119 (100), 102 (6), 92 (10), 91 (48).

$C_{41}H_{30}N_6O_5$ (686.7) Calcd. C 71.71 H 4.40 N 12.24
Found C 71.39 H 4.67 N 11.86

As the last eluate 180 mg (4%) of an as yet unknown cycloadduct was obtained as colorless needles, m.p. 189–191°C (acetone).

Cycloaddition of PTAD to **2d**: From the reaction mixture of 3.00 g (9.80 mmol) of **2d** with 1.90 g (10.9 mmol) of PTAD at room temp. for 24 h 1.42 g (47%) of **2d** was recovered as first eluate. As second eluate 750 mg (29%, based on the substrate consumed) of cycloadduct **3d** was isolated in form of colorless prisms, m.p. 182–184°C (ethanol) (ref.[2]) m.p. 183–184°C). – ^1H NMR ($CDCl_3$, 60 MHz): δ = 3.87 (m, 1H, 13-H), 4.28 (m, 1H, 6-H), 4.82 (m, 1H, 1-H), 5.23 (m, 1H, 4-H), 6.90–7.36 (m, 19H, aromatic H).

As the third eluate 350 mg (10%) of cycloadduct *syn/syn*-**4d** was obtained in form of colorless prisms, m.p. 205–207°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3030, 2920, 1788, 1766, 1725, 1709, 1503, 1402, 1250, 1139, 758, 731, 700, 690. – ^1H NMR (C_6D_6, 200 MHz): δ = 3.92 (m, $J_{3',4'}$ = 3.2, $J_{1',4'}$ = 1.9, $J_{2',4'}$ = 1.0, $J_{4',5'}$ = 0.5 Hz, 1-H, 4′-H), 4.14 (d, $J_{1,2}$ = 2.2 Hz, 1H, 2-H), 4.75 (m, $J_{1',2'}$ = 3.1,

$J_{1',4'}$ = 1,9, $J_{1',3'}$ = 1.0, $J_{1',8'}$ = 0.5 Hz, 1H, 1'-H), 5.19 (dd, $J_{8,12}$ = 5.0, $J_{8,11}$ = 2.2 Hz, 1H, 8-H), 5.68 (ddd, $J_{2',3'}$ = 5.6, $J_{1',2'}$ = 3.1, $J_{2',4'}$ = 1.0 Hz, 1H, 2'-H), 5.79 (AB system, $J_{11,12}$ = 8.0, $J_{8,12}$ = 5.0, $J_{1,12}$ = 2.2 Hz, 1H, 12-H), 5.85 (AB system, $J_{11,12}$ = 8.0, $J_{1,11}$ = 5.8, $J_{8,11}$ = 2.2 Hz, 1H, 11-H), 6.04 (ddd, $J_{2',3'}$ = 5.6, $J_{3',4'}$ = 3.2, $J_{1',3'}$ = 1.0 Hz, 1H, 3'-H), 6.69 (m, 1H, *ortho*-H of 6-phenyl), 6.76 (ddd, $J_{1,11}$ = 5.8, $J_{1,2}$ = $J_{1,12}$ = 2.2 Hz, 1H, 1-H), 6.79–7.18 (m, 15H, aromatic H), 7.22 (m, 1H, 5'-H), 7.38 (m, 1H, *ortho*-H of 6-phenyl), 7.50 (m, 1H, 8'-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.0 (d), 51.6 (d), 54.1 (d), 56.9 (d), 58.0 (d), 94.4 (s), 122.4 (d), 124.6 (d), 125.2 (d), 125.3 (d), 125.7 (d), 127.0 (d), 127.8 (d), 128.2 (d), 128.2 (d), 128.5 (d), 128.8 (d), 129.0 (d), 129.6 (d), 130.2 (d), 131.2 (d), 137.5 (s), 138.4 (d), 143.1 (d), 145.6 (s), 145.9 (s), 146.0 (s), 147.0 (s), 149.6 (s), 154.3 (s), 155.9 (s). – MS (70 eV): *m/z* (%) = 656 (0.2) [M$^+$], 479 (2), 353 (3), 306 (11), 129 (11), 128 (100), 127 (13), 119 (14), 102 (10).

$C_{40}H_{28}N_6O_4$ (656.7) Calcd. C 73.16 H 4.30 N 12.80
Found C 72.74 H 4.02 N 12.69

As third eluate 430 mg (13%) of cycloadduct *syn/anti*-**4d** was obtained in form of colorless prisms, m.p. 219–222°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 2920, 1783, 1765, 1722, 1600, 1502, 1458, 1405, 1292, 1245, 1187, 1137, 1025, 772, 747, 703, 645. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 4.14 (m, $J_{3',4'}$ = 3.2, $J_{1',4'}$ = 2.0, $J_{2',4'}$ = 1.0, $J_{4',5'}$ = 0.5 Hz, 1H, 4'-H), 4.75 (d, $J_{1,2}$ = 3.0 Hz, 1H, 2-H), 4.95 (m, $J_{1',2'}$ = 3.3, $J_{1',4'}$ = 2.0, $J_{1',3'}$ = 1.1, $J_{1',8'}$ = 0.5 Hz, 1H, 1'-H), 5.39 (dd, $J_{8,12}$ = 6.0, $J_{8,11}$ = 2.0 Hz, 1H, 8-H), 5.45 (ddd, $J_{11,12}$ = 7.4, $J_{8,12}$ = 6.0, $J_{1,12}$ = 1.5 Hz, 1H, 12-H), 5.69 (ddd, $J_{2',3'}$ = 5.6, $J_{1',2'}$ = 3.3, $J_{2',4'}$ = 1.0 Hz, 1H, 2'-H), 6.05 (ddd, $J_{11,12}$ = 7.4, $J_{1,11}$ = 5.4, $J_{8,11}$ = 2.0 Hz, 1H, 11-H), 6.10 (ddd, $J_{2',3'}$ = 5.6, $J_{3',4'}$ = 3.2, $J_{1',3'}$ = 1.1 Hz, 1H, 3'-H), 6.58 (ddd, $J_{1,11}$ = 5.4, $J_{1,2}$ = 3.0, $J_{1,12}$ = 1.5 Hz, 1H, 1-H), 6.78–7.05 (m, 13H, aromatic H), 7.07 (m, 1H, *ortho*-H of 6-phenyl), 7.17 (m, 1H, *ortho*-H of 6-phenyl), 7.28 (m, 1H, 5'-H), 7.48 (m, 1H, 8'-H), 7.60 (m, 2H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.1 (d), 52.8 (d), 54.6 (d), 55.3 (d), 59.0 (d), 94.5 (s), 122.4 (d), 124.1 (d), 125.3 (d), 125.4 (d), 125.7 (d), 126.8 (d), 127.6 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.7 (d), 130.4 (d), 131.0 (d), 131.2 (d), 137.3 (s), 138.2 (d), 141.4 (s), 142.7 (d), 146.6 (s), 147.0 (s), 150.0 (s), 155.1 (s), 155.3 (s). – MS (70 eV): *m/z* (%) = 656 (0.1) [M$^+$], 481 (8), 479 (13), 353 (31), 321 (23), 306 (16), 304 (14), 234 (14), 206 (15), 178 (18), 177 (52), 143 (15), 128 (19), 120 (31), 119 (100).

$C_{40}H_{28}N_6O_4$ (656.7) Calcd. C 73.16 H 4.30 N 12.80
Found C 73.28 H 4.14 N 12.52

Cycloaddition of 4-Methyl-4H-1,2,4-triazole-3,5-dione (MTAD) *to* **2d**: From the reaction mixture of 3.00 g (9.79 mmol) of **2d** with 2.26 g (20.0 mmol) of MTAD in dichloromethane at 42°C for 20 h the following products were isolated.

1.05 g (26%) of cycloadduct **3d** (NMe instead of NPh) was obtained as the first eluate in form of colorless prisms, m.p. 239–240°C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1}, 3075, 3040, 2962, 1782, 1720, 1495, 1455, 1397, 1210, 1032, 765, 707. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.13 (s, 3H, NCH_3), 3.71 (m, 1H, 13-H), 4.16 (m, 1H, 6-H), 4.73 (m, 1H, 1-H), 5.09 (m, 1H, 4-H), 6.91–7.43 (m, 14H, aromatic H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.6 (q), 52.6 (d), 53.9 (d), 62.3 (d), 77.2 (d), 121.1 (d), 123.7 (d), 127.1 (d), 127.4 (d), 128.0 (d), 128.3 (d), 128.9 (d), 129.0 (d), 134.0 (s), 136.2 (s), 140.2 (s), 140.7 (s), 143.2 (s), 157.6 (s), 158.5 (s). – MS (70 eV): *m/z* (%) = 421 (3) [M + 2], 420 (17) [M + 1], 419 (57) [M$^+$], 418 (4), 342 (14), 306 (18), 305 (66), 304 (100), 303 (40), 292 (12), 291 (14), 290 (11), 289 (14), 215 (33), 191 (12), 165 (11), 115 (11).

$C_{27}H_{21}N_3O_2$ (419.5) Calcd. C 77.31 H 5.05 N 10.02
Found C 77.40 H 5.06 N 10.22

As second eluate 1.10 g (21%) of cycloadduct *syn/anti*-**4d** (NMe instead of NPh) was obtained in form of colorless prisms, m.p. 187.5–188.5°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3092 cm^{-1}, 3060, 3035, 2955, 1790, 1768, 1728, 1715, 1457, 1397, 1266, 1190, 1000, 925, 790, 750, 705, 650. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.82 (s, 3H, NCH_3), 3.01 (s, 3H, NCH_3), 4.45 (m, 1H, 4'-H), 4.71 (m, 1H, 1'-H), 5.05 (d, $J_{1,2}$ = 1.5 Hz, 1H, 2-H), 5.16 (dd, $J_{8,12}$ = 4.0, $J_{8,11}$ = 1.8 Hz, 1H, 8-H), 6.01 (ddd, $J_{2',3'}$ = 5.0, $J_{1',2'}$ = 3.3, $J_{2',4'}$ = 0.6 Hz, 1H, 2'-H), 6.17–6.30 (m, 3H, 1-, 11-, 12-H), 6.57 (ddd, $J_{2',3'}$ = 5.0, $J_{3',4'}$ = 3.5, $J_{1',3'}$ = 0.5 Hz, 1H, 3'-H), 6.94–7.50 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.1 (q), 25.6 (q), 52.0 (d), 52.7 (d), 54.5 (d), 55.0 (d), 58.9 (d), 94.2 (s), 122.3 (d), 123.8 (d), 125.1 (d), 125.6 (d), 126.7 (d), 127.3 (d), 127.8 (d), 128.4 (d), 128.9 (d), 129.9 (s), 130.4 (d), 137.3 (s), 138.2 (d), 140.7 (s), 142.7 (d), 146.7 (s), 149.2 (s), 151.2 (s), 156.8 (s), 157.0 (s). – MS (70 eV): *m/z* (%) = 533 (0.2) [M + 1], 532 (0.6) [M$^+$], 419 (0.9), 418 (0.7), 417 (1), 291 (9), 129 (11), 128 (100), 127 (13).

$C_{30}H_{24}N_6O_4$ (532.6) Calcd. C 67.66 H 4.54 N 15.78
Found C 67.48 H 4.60 N 15.90

As third eluate 850 mg (16%) of cycloadduct *syn/syn*-**4d** (NMe instead of NPh) was obtained in form of colorless prisms, m.p. 209–210°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3030, 2950, 1780, 1760, 1720, 1450, 1390, 1260, 1195, 1035, 1005, 910, 790, 738, 702, 636. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.87 (s, 3H, NCH_3), 2.91 (s, 3H, NCH_3), 4.27 (m, 1H, 4'-H), 4.64 (d, $J_{1,2}$ = 2.3 Hz, 1H, 2-H), 4.67 (m, 1H, 1'-H), 5.07 (dd, $J_{8,12}$ = 3.8, $J_{8,11}$ = 3.3 Hz, 1H, 8-H), 6.03 (ddd, $J_{2',3'}$ = 5.6, $J_{1',2'}$ = 3.3, $J_{2',4'}$ = 0.9 Hz, 1H, 2'-H), 6.43–6.59 (m, 4H, 1-, 3'-, 11-, 12-H), 6.91–7.05 (m, 3H, aromatic H), 7.13–7.48 (m, 6H, aromatic H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.3 (q), 25.5 (q), 50.6 (d), 51.4 (d), 54.2 (d), 56.2 (d), 58.1 (d), 93.7 (s), 122.3 (d), 124.1 (d), 125.0 (d), 125.7 (d), 126.9 (d), 128.1 (d), 128.4 (d), 128.7 (d), 129.4 (d), 130.2 (d), 130.7 (d), 137.4 (s), 138.3 (d), 143.1 (d), 144.6 (s), 146.4 (s), 146.9 (s), 147.3 (s), 151.0 (s), 156.1 (s), 157.7 (s). – MS (70 eV): *m/z* (%) = 534 (0.3) [M + 2], 533 (2) [M + 1], 532 (5) [M$^+$], 419 (6), 418 (15), 417 (22), 361 (6), 331 (7), 319 (7), 305 (10), 291 (13), 165 (8), 152 (7), 128 (17), 46 (18), 45 (44), 31 (100).

$C_{30}H_{24}N_6O_4$ Calcd. 532.1859 Found 532.1863 (MS)

The X-ray results are given in Tables 2 and 4, and the structure is exhibited in Figure 1.

Cycloaddition of PTAD to **2e**: From the reaction mixture of 1.90 g (5.06 mmol) of **2e** with 1.77 g (10.1 mmol) of PTAD at room temp. for 24 h 990 mg (36%) of **3e** was obtained as the first eluate in form of colorless needles, m.p. 158–161°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 3040, 1786, 1711, 1510, 1492, 1422, 1298, 1272, 1250, 1232, 1138, 1091, 1019, 827, 815, 770, 758, 730, 695. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.87 (m, 1H, 13-H), 4.25 (m, 1H, 6-H), 4.86 (ddd, $J_{1,13}$ = 2.5, $J_{1,6}$ = 2.0, $J_{1,4}$ = 0.5 Hz, 1H, 1-H), 5.15 (dd, $J_{4,13}$ = 2.0, $J_{1,4}$ = 0.5 Hz, 1H, 4-H), 6.93–7.70 (m, 17H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.8 (d), 54.1 (d), 62.8 (d), 77.2 (d), 121.2 (d), 124.1 (d), 125.3 (d), 127.6 (d), 128.5 (d), 128.6 (d), 128.9 (d), 129.3 (d), 130.4 (d), 130.5 (d), 131.6 (s), 134.0 (s), 135.4 (s), 136.1 (s), 137.3 (s), 138.4 (s), 138.7 (s), 142.9 (s), 155.7 (s), 156.5 (s). – MS (70 eV): *m/z* (%) = 553 (7) [M + 4], 551 (38) [M + 2], 550 (20) [M + 1], 549 (57) [M$^+$], 388 (24), 375 (29), 374 (76), 373 (41), 372 (100), 340 (17), 339 (36), 338 (43), 337 (47), 327 (15), 326 (19), 325 (37), 302 (47), 119 (60).

$C_{32}H_{21}Cl_2N_3O_2$ (550.4) Calcd. C 69.83 H 3.85 N 7.64
Found C 69.66 H 3.82 N 7.54

As the second eluate 202 mg (6%) of cycloadduct *syn/syn*-**4e** was obtained in form of a colorless powder, m.p. 204–205°C (ethan-

ol). – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1}, 3050, 1790, 1762, 1730, 1705, 1608, 1502, 1460, 1400, 1235, 1220, 1138, 1092, 1055, 1015, 780, 765, 747, 700, 690, 645. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.36 (m, 1H, 4′-H), 4.63 (m, 1H, 1′-H), 4.98 (d, $J_{1,2}$ = 2.2 Hz, 1H, 2-H), 5.22 (d, $J_{8,12}$ = 6.1 Hz, 1H, 8-H), 6.17 (ddd, $J_{2',3'}$ = 5.5, $J_{1',2'}$ = 3.5, $J_{2',4'}$ = 1.0 Hz, 1H, 2′-H), 6.50 (ddd, $J_{2',3'}$ = 5.5, $J_{3',4'}$ = 3.5, $J_{1',3'}$ = 1.0 Hz, 1H, 3′-H), 6.56 (dd, $J_{8,12}$ = 6.1, $J_{1,12}$ = 2.2 Hz, 1H, 12-H), 6.68 (dd, $J_{1,2}$ = $J_{1,12}$ = 2.2 Hz, 1H, 1-H), 6.93–7.70 (m, 18H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.5 (d), 54.1 (d), 56.9 (d), 58.0 (d), 58.4 (d), 94.0 (s), 122.6 (d), 124.7 (d), 125.3 (d), 125.4 (d), 125.5 (d), 125.7 (d), 125.9 (d), 126.3 (d), 127.9 (d), 128.3 (d), 128.5 (d), 128.9 (d), 129.0 (d), 129.1 (d), 131.0 (s), 131.2 (s), 131.6 (d), 132.6 (s), 134.6 (s), 135.7 (s), 138.6 (d), 143.2 (d), 144.8 (s), 145.8 (s), 145.9 (s), 146.6 (s), 149.6 (s), 154.4 (s), 155.4 (s). – MS (70 eV): *m/z* (%) = 549 (1) [M – PTAD], 322 (11), 305 (13), 304 (78), 303 (73), 302 (39), 128 (47), 120 (17), 119 (100).

$C_{40}H_{26}Cl_2N_6O_4$ (725.6) Calcd. C 66.21 H 3.61 N 11.58
Found C 66.22 H 3.78 N 11.56

As third eluate 154 mg (4%) of cycloadduct *syn/anti*-**4e** was isolated in form of a colorless powder, m.p. 210–211 °C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 1790, 1770, 1735, 1720, 1705, 1600, 1505, 1492, 1458, 1408, 1250, 1138, 1095, 778, 758, 738, 703, 690, 650. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 4.43 (m, 1H, 4′-H), 4.56 (m, 1H, 1′-H), 5.24 (d, $J_{8,12}$ = 6.5 Hz, 1H, 8-H), 5.25 (d, $J_{1,2}$ = 2.5 Hz, 1H, 2-H), 6.14 (ddd, $J_{2',3'}$ = 5.5, $J_{1',2'}$ = 3.5, $J_{2',4'}$ = 1.0 Hz, 1H, 2′-H), 6.35 (dd, $J_{8,12}$ = 6.5, $J_{1,12}$ = 2.5 Hz, 1H, 12-H), 6.63 (ddd, $J_{2',3'}$ = 5.5, $J_{3',4'}$ = 3.5, $J_{1',3'}$ = 1.0 Hz, 1H, 3′-H), 6.75 (dd, $J_{1,2}$ = $J_{1,12}$ = 2.5 Hz, 1H, 1-H), 6.96–7.54 (m, 18H, aromatic H). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 54.0 (d), 54.1 (d), 55.2 (d), 57.1 (d), 59.0 (d), 94.0 (s), 96.2 (s), 122.6 (d), 124.8 (d), 125.3 (d), 125.5 (d), 126.0 (d), 126.6 (d), 128.1 (d), 128.3 (d), 128.7 (d), 128.9 (d), 129.0 (d), 129.3 (d), 129.6 (d), 130.8 (s), 131.0 (s), 131.8 (d), 134.6 (s), 135.8 (s), 138.7 (d), 142.2 (s), 142.9 (d), 145.4 (s), 145.6 (s), 146.6 (s), 149.1 (s), 154.9 (s), 155.4 (s). – MS (70 eV): *m/z* (%) = 550 (0.1) [M – PTAD], 549 (0.4), 423 (1), 421 (1), 304 (1), 303 (1), 302 (1), 129 (11), 128 (100), 127 (13), 126 (8), 119 (14), 102 (10), 101 (3), 91 (8).

$C_{40}H_{26}Cl_2N_6O_4$ (725.6) Calcd. C 66.21 H 3.61 N 11.58
Found C 66.09 H 3.38 N 11.73

Cycloaddition of PTAD to **2f**: From the reaction mixture of 1.19 g (3.39 mmol) of **2f** with 1.19 g (6.83 mmol) of PTAD in dichloromethane at 42 °C for 5 h the following products were isolated.

420 mg (24%) of cycloadduct *E*-**3f** was isolated as the first eluate in form of pale yellow needles, m.p. 264–265 °C (acetone). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3012, 3008, 1786, 1725, 1600, 1520, 1502, 1408, 1395, 1340, 1228, 1132, 1082, 852, 761, 751, 725, 708, 690. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.88 (m, 1H, 13-H), 4.21 (m, 1H, 6-H), 4.91 (ddd, $J_{1,13}$ = 2.6, $J_{1,6}$ = 2.1, $J_{1,4}$ = 0.8 Hz, 1H, 1-H), 5.24 (dd, $J_{4,13}$ = 2.1, $J_{1,4}$ = 0.8 Hz, 1H, 4-H), 6.95 (m, 1H, 8-H), 7.09 (m, 2H, 2″-, 6″-H), 7.23–7.57 (m, 13H, aromatic H), 8.27 (d, *J* = 8.7 Hz, 2H, 3′-, 5′-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.8 (d), 54.0 (d), 62.8 (d), 77.6 (d), 121.1 (d), 123.8 (d), 124.3 (d), 125.2 (d), 127.8 (d), 128.3 (d), 128.5 (d), 128.6 (d), 129.2 (d), 129.3 (d), 130.1 (d), 131.7 (s), 136.2 (s), 136.4 (s), 137.6 (s), 139.1 (s), 142.5 (s), 147.4 (s), 155.6 (s), 156.6 (s). – MS (70 eV): *m/z* (%) = 527 (30) [M^+], 526 (82), 449 (6), 407 (11), 390 (20), 365 (25), 364 (15), 351 (17), 350 (52), 349 (100), 303 (48), 289 (37), 215 (47), 119 (31).

$C_{32}H_{22}N_4O_4$ (526.6) Calcd. C 72.99 H 4.21 N 10.64
Found C 72.84 H 4.10 N 10.97

310 mg (17%) of cycloadduct *Z*-**3f** was obtained as the second eluate, pale yellow needles, m.p. 199–201 °C (acetone). – IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 3025, 1780, 1715, 1598, 1510, 1420, 1345, 1228, 1145, 1105, 1090, 782, 768, 757, 728, 700. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 3.94 (m, 1H, 13-H), 4.34 (m, 1H, 6-H), 4.88 (ddd, $J_{1,13}$ = 2.7, $J_{1,6}$ = 2.1, $J_{1,4}$ = 0.8 Hz, 1H, 1-H), 5.16 (dd, $J_{4,13}$ = 2.1, $J_{1,4}$ = 0.8 Hz, 1H, 4-H), 6.94 (m, 1H, 8-H), 7.06 (m, 2H, 2″-, 6″-H), 7.21–7.56 (m, 13H, aromatic H), 8.14 (d, *J* = 8.9 Hz, 2H, 3′-, 5′-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 53.1 (d), 54.3 (d), 62.7 (d), 77.2 (d), 121.6 (d), 123.6 (d), 124.2 (d), 125.3 (d), 127.8 (d), 128.4 (d), 128.7 (d), 129.0 (d), 129.4 (d), 130.2 (d), 131.6 (s), 136.1 (s), 137.7 (s), 137.8 (s), 139.5 (s), 142.7 (s), 146.9 (s), 147.4 (s), 155.7 (s), 156.3 (s). – MS (70 eV): *m/z* (%) = 527 (31) [M^+], 526 (85), 449 (6) [M – C_6H_6], 350 (50), 349 (100), 304 (30), 303 (44), 291 (31), 289 (37), 215 (49), 119 (30).

$C_{32}H_{22}N_4O_4$ (526.6) Calcd. C 72.99 H 4.21 N 10.64
Found C 72.74 H 3.99 N 10.60

106 mg (5%) of cycloadduct *syn/syn*-**4f** were obtained as the third eluate in form of a colorless powder, m.p. 207–209 °C (acetone). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 1788, 1762, 1725, 1705, 1599, 1515, 1500, 1400, 1345, 752, 732, 708, 690. – ^1H NMR (C_6D_6, 200 MHz): δ = 3.86 (m, 1H, 4′-H), 4.10 (d, $J_{1,2}$ = 2.2 Hz, 1H, 2-H), 4.51 (m, 1H, 1′-H), 4.96 (m, 1H, 8-H), 5.39 (ddd, $J_{2',3'}$ = 5.6, $J_{1',2'}$ = 3.3, $J_{2',4'}$ = 1.1 Hz, 1H, 2′-H), 5.88 (m, 2H, 11-, 12-H), 5.94 (ddd, $J_{2',3'}$ = 5.6 Hz, $J_{3',4'}$ = 3.4, $J_{1',3'}$ = 1.0 Hz, 1H, 3′-H), 6.29 (m, 1H, *ortho*-H *p*-$NO_2C_6H_4$), 6.73 (m, 1H, 1-H), 6.78–7.24 (m, 13H, aromatic H), 7.42 (m, 1H, aromatic H), 7.54 (m, 1H, 8′-H), 7.79 (m, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 51.0 (d), 51.6 (d), 54.0 (d), 57.1 (d), 58.2 (d), 94.0 (s), 122.6 (d), 123.8 (d), 124.1 (d), 124.8 (d), 125.3 (d), 125.5 (d), 125.8 (d), 126.0 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.9 (d), 129.1 (d), 130.1 (d), 130.6 (d), 131.5 (d), 139.4 (d), 143.0 (d), 143.7 (d), 144.0 (s), 145.4 (s), 146.2 (s), 146.4 (s), 147.6 (s), 149.6 (s), 154.4 (s), 155.7 (s). – MS (70 eV): *m/z* (%) = 524 (0.03), 351 (1), 322 (1), 178 (1), 177 (10), 129 (11), 128 (100), 127 (13), 126 (8), 120 (6), 119 (31), 102 (10), 91 (17).

$C_{40}H_{27}N_7O_6$ (701.7) Calcd. C 68.47 H 3.88 N 13.97
Found C 68.09 H 4.15 N 13.52

160 mg (7%) of cycloadduct *syn/anti*-**4f** was obtained as the fourth eluate in form of a colorless powder, m.p. 218–219 °C (acetone). – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3030, 2950, 1782, 1760, 1730, 1705, 1600, 1525, 1490, 1392, 1350, 1240, 1220, 1138, 770, 755, 748, 710, 690, 642. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.54 (m, 1H, 4′-H), 4.75 (m, 1H, 1′-H), 5.22 (m, 2H, 2-, 8-H), 6.06 (ddd, $J_{2',3'}$ = 5.8, $J_{1',2'}$ = 3.5, $J_{2',4'}$ = 1.0 Hz, 1H, 2′-H), 6.37 (m, 1H), 6.47 (m, 2H), 6.66 (ddd, $J_{2',3'}$ = 5.8, $J_{3',4'}$ = 3.5, $J_{1',3'}$ = 1.0 Hz, 1H, 3′-H), 7.05 (m, 2H, aromatic H), 7.21–7.49 (m, 14H, aromatic H), 8.31 (dd, *J* = 8.5, *J* = 2.3 Hz, 1H, aromatic H), 8.36 (dd, *J* = 8.5, *J* = 2.3 Hz, 1H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.1 (d), 52.7 (d), 54.5 (d), 55.4 (d), 59.3 (d), 94.1 (s), 122.7 (d), 124.1 (d), 124.3 (d), 125.3 (d), 125.4 (d), 125.7 (d), 126.0 (d), 127.9 (d), 128.3 (d), 128.4 (d), 128.6 (d), 129.0 (d), 129.2 (d), 130.3 (d), 131.8 (d), 139.2 (d), 139.4 (s), 142.6 (d), 143.6 (s), 146.0 (s), 147.4 (s), 147.6 (s), 150.1 (s), 155.2 (s), 155.3 (s). – MS (70 eV): *m/z* (%) = 526 (1) [M – PTAD], 449 (1), 404 (2), 398 (2), 178 (2), 177 (21), 129 (11), 128 (100), 127 (13), 120 (13), 119 (58), 102 (9), 91 (29).

$C_{40}H_{27}N_7O_6$ (701.7) Calcd. C 68.47 H 3.88 N 13.97
Found C 68.36 H 4.36 N 13.29

CAS Registry Numbers

1a: 7738-50-3 / **1b**: 2320-32-3 / **1c**: 16146-07-9 / **1d**: 2175-90-8 / **1e**: 15999-71-0 / **1f**: 6602-76-2 / **2a**: 67654-88-0 / **2b**: 116971-99-4 / **2c**: 116972-00-0 / **2d**: 28591-78-8 / **2e**: 116972-01-1 / **2f**: 116972-02-2 / (±)-**3a**: 116972-03-3 / (±)-**3b**: 116972-04-4 / (+)-(*E*)-**3c**: 116972-05-5 / (±)-(*Z*)-**3c**: 116972-06-6 / (±)-**3d** (NPh): 116972-09-9 / (±)-**3d** (NMe): 116972-11-3 / (±)-**3e**: 116972-13-5 / (±)-(*E*)-

3i: 116972-15-7 / (±)-(*Z*)-**3f**: 116972-16-8 / **4c**: 116972-08-8 / (±)-**4d** (NPh), isomer 1: 116972-10-2 / (±)-**4d** (NPh), isomer 2: 117064-18-3 / (±)-**4d** (NMe), isomer 1: 116972-12-4 / (±)-**4d** (NMe), isomer 2: 117064-19-4 / (±)-**4e**, isomer 1: 116972-14-6 / (±)-**4e**, isomer 2: 117064-20-7 / (±)-**4f**, isomer 1: 116972-17-9 / (±)-**4f**, isomer 2: 117064-21-8 / (±)-**5c**: 116972-07-7 / PTAD: 4233-33-4 / MTAD: 13274-43-6 / anthranilic acid: 118-92-3 / benzyne: 462-80-6

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