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Photochemistry of Tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene Based Systems**

Bulusu A. R. C. Murty, Paul R. Spurr, Rolf Pinkos, Clemens Grund, Wolf-Dieter Fessner, Dieter Hunkler, Hans Fritz, Wolfgang R. Roth*, and Horst Prinzbach*

Abstract: The feasibility of intramolecular [2+2]- and [6+2]- or [6+6]-photocycloaddition reactions in tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecadienes and mono- or bis-benzoanellated systems as well as the stability of the respective photoisomers are discussed on the basis of structural and calculated thermochemical data. Sensitized excitation of conformationally modified dienes of type **B-1** (see Scheme 1) yields, uniformly, the stable [2+2]-adducts. [6+2]-additions in benzo-enes **B-2** are observed upon direct excitation and on account of their thermal lability, the photoproducts were only characterized indirectly. At temperatures down to −75°C, no [6+6]-adduct formation has been observed in **B-3** face-to-face dibenzo substrates.

In the 1,6-dichromophoric series «**A**» (Scheme 1), transannular ene/ene (**A-1**)[2], benzo/ene (**A-2**)[3], and benzo/benzo interactions (**A-3**)[1,3] as well as transannular bond formations have been intensively studied. Variation of the geometrical/stereoelectronic situations has been introduced by altering the nature of the bridges X. A prominent example is the benzo/benzo [6+6]-photocycloaddition **1**→**2** (Scheme 2) which has allowed the construction of pagodanes **3** ([2.2.1.1]-pagodadiene) and **4** ([1.1.1.1]pagodane)[4] and of bissecododecahedradienes **5**[5]. Such undeca-/nonacyclic, conformationally very rigid and highly strained hydrocarbons serve as intermediates on the way to dodecahedrane-type structures and, because of their tendency for one-/two-electron oxidations, as precursors for unusually stable radical cations **6**[6] and novel 2π-aromatic cyclobutanoid dications **7**[7], respectively (Scheme 3).

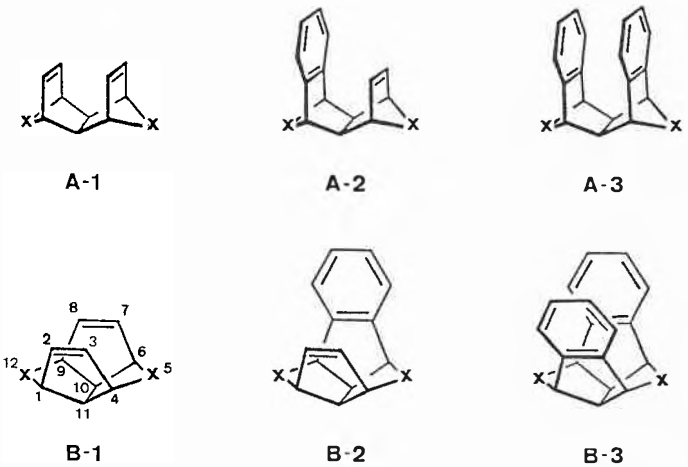
It was i.a. the interest in the structure/stability relationship of these (radical) cations with those (**13** and **14**, Scheme 3) derived from the D_{2d} «isopagodane» **11** and its unique diene-derivative **12** which stimulated the synthesis of **11** and **12** via the sequence **8**→**9**→**10**→**11**→**12** (Scheme 2). This approach was patterned on the one worked out for **4** and **5** and features the benzo/benzo-photocycloaddition **8**→**9** as a key step.

In this context, we started a systematic photochemical study with dienes of type **B-1** (**18a–d**; **20a, b**; **34**; **44**), with benzo-enes of type **B-2** (**29a, b**), and with (hetero) dibenzo-substrates of type **B-3** (**8a–d**; **42**) or **A-3** (**40**). The main photochemical results as well as their correlation with MM2-derived thermochemical data for the isomeric series **A**/**B** are presented in this communication[8].

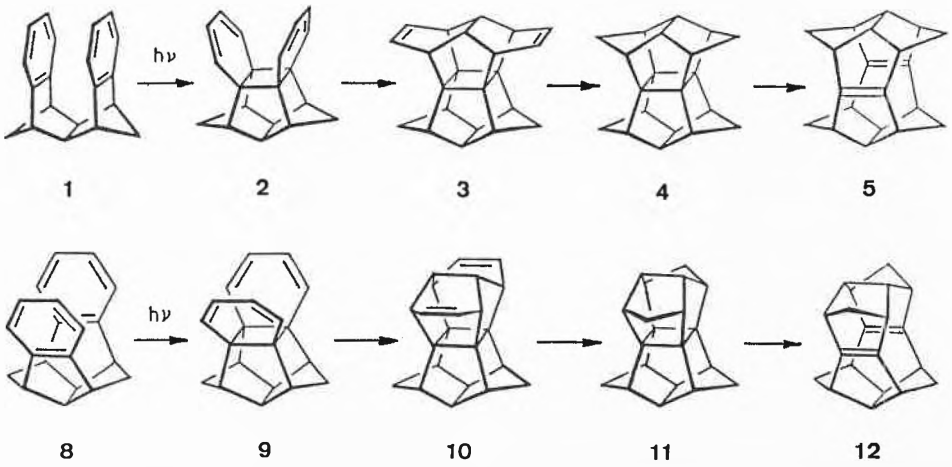
1. *Ene/Ene-Cycloadditions (***B-1***)*

In contrast to the rigid frameworks of the dienes **A-1**, the **B-1** isomers are conformationally more mobile with the «closed»/«open» geometries **18′/18″**, according to the MM2 force-field calculations[9], representing energy minima (Scheme 4). In the higher-energy minima **18″**, photo-[2+2]-additions are obviously not possible.

Scheme 1



Scheme 2



* *Correspondence:* Prof. Dr. Prinzbach
Institut für Organische Chemie und Biochemie
Universität Freiburg
Albertstrasse 21, D–7800 Freiburg i. Br.
(Bundesrepublik Deutschland)

Prof. Dr. W. R. Roth
Institut für Organische Chemie I
Ruhr-Universität Bochum

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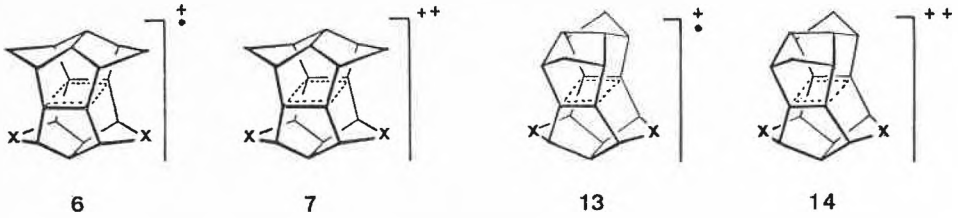
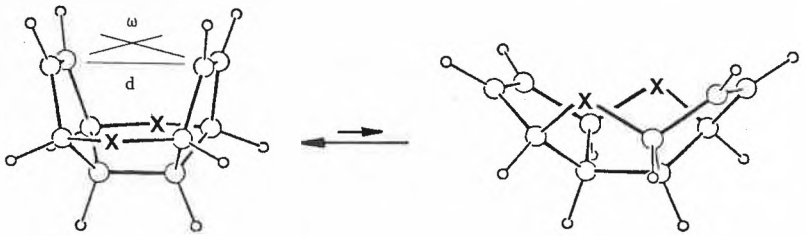
Scheme 3



6 7 13 14

Scheme 4

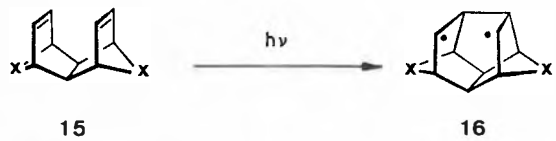


18' 18''

ΔH_f° :	31.1 (X=CH_2)	34.3
d(Å):	3.10	4.68
ω(°):	153.3	74.0

	a	b	c	d
X	CH_2	$C(OCH_2)_2$	C=O	$C=C(CN)_2$

Scheme 5



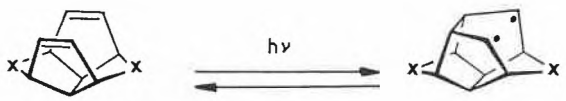
15 16

	ΔH_f°	d	ω
a	56.0	2.78	176.5
e	35.1	2.72	180.0
f	106.3	2.83	174.1

	ΔH_f°
a	100.9
e	77.1
f	148.7

17

	ΔH_f°
a	27.2
e	1.1
f	77.9



18 19

	ΔH_f°	d	ω
a	31.1	3.10	153.3
e	3.8	3.17	150.0
f	76.2	3.42	142.2

	ΔH_f°
a	86.4
e	59.9
f	133.8

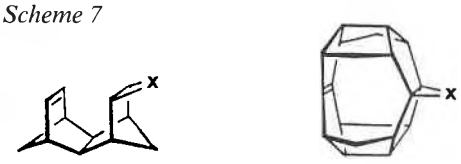
	a	b	c	d	e	f
X	CH_2	$C(OCH_2)_2$	C=O	$C=C(CN)_2$	$C(CH_3)_2$	$C=CH_2$

In Scheme 5, the calculated thermochemical and structural data for the rigid diene **15a**[10], its (rapidly formed) [2+2]-adduct **17a**, and the potential diradical intermediate **16a** are compared with those for the diene **18a** and the corresponding diradical intermediate **19a**. The 5,12-bis(dimethyl) and bis(methylene) derivatives serve as prototypes of the bisacetal **18b**[11], the diketone **18c**[12], and the bis(dicyanomethylene) compound **18d**. As suggested from consideration of models and ^{1}H-NMR analysis (i.a. $J_{1,12\alpha} = 8$, $J_{1,12\beta} \approx 0$ Hz), the «closed» conformations are clearly favored; the methyl substituents at C-5/C-12 exert a minimal, sp^2-hydridization a more pronounced shift towards **18''**. These data make it clear why the highly strained cage **17a** is kinetically very stable and why exclusively b-bonds are broken to give diene **18a**.

Concerning the photochemical cyclobutane formation in **18a–d**, the chances were considered very promising in the cases of **18a, b** and somewhat less so in the cases of **18c, d** as judged by the relevant criteria (transannular distance *d*, interorbital angle ω, and differential ΔH_f^0 values[13]) though overall, cyclization in these systems seemed not as favorable as for **15a**→**17a**. In sensitized excitation experiments with **18a–d** (10^{-3} M degassed acetone solution, pyrex filter glass, 150 W high pressure Hg lamp, 20°C), uniform transformations proceeded, to give the cage compounds **17a–d** in practically quantitative yield, independent of the somewhat lower rate in the cases of **18c, d**[14].

In the bissecododecahedradienes **20a, b**[15] (Scheme 6; see page 34), the («closed») diene (dione)-units of **18a, c** are part of a very rigid molecular framework, with the consequence that the π/π-distance becomes even shorter than in **18'** and the interorbital angle ω reaches the optimal 180°. According to calculations, the [2+2]-cycloaddition in **20a** to give the pagodane **22a** is, in contrast to **18**→**17**, slightly endothermic. Under the sensitized conditions used for **18a–d**, the photocycloadditions **20a, b**→**22a, b** were again uniform. In view of the ideal orbital alignment in the homoenes **24** (X = CHR, O, NR), photo-[2π+2σ]-additions (Scheme 7), which occur only sluggishly in substrates of type **23**[3,16], should be achievable.

Scheme 7



23 24

2. *Benzo/Ene-Cycloadditions (***B-2***)*

For the benzo-enes **29**, with *d* and ω values comparable to the ones in the dienes **18**, preference for the «closed» conforma-

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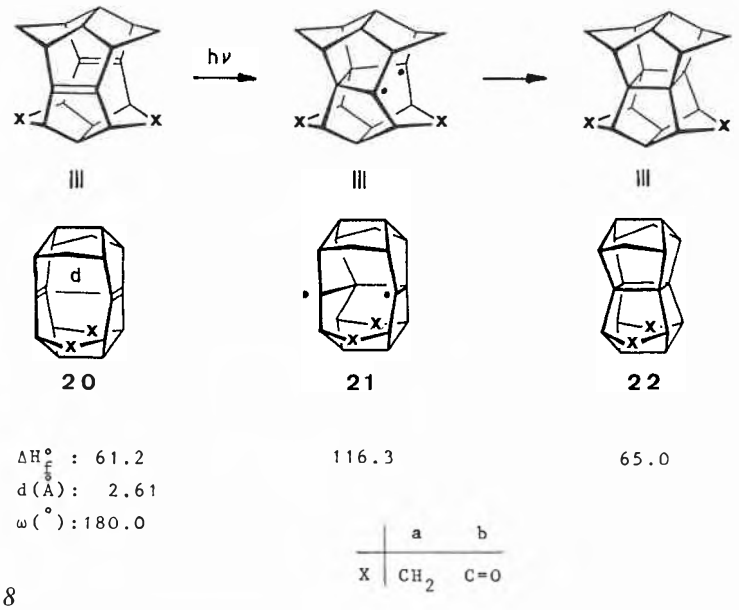
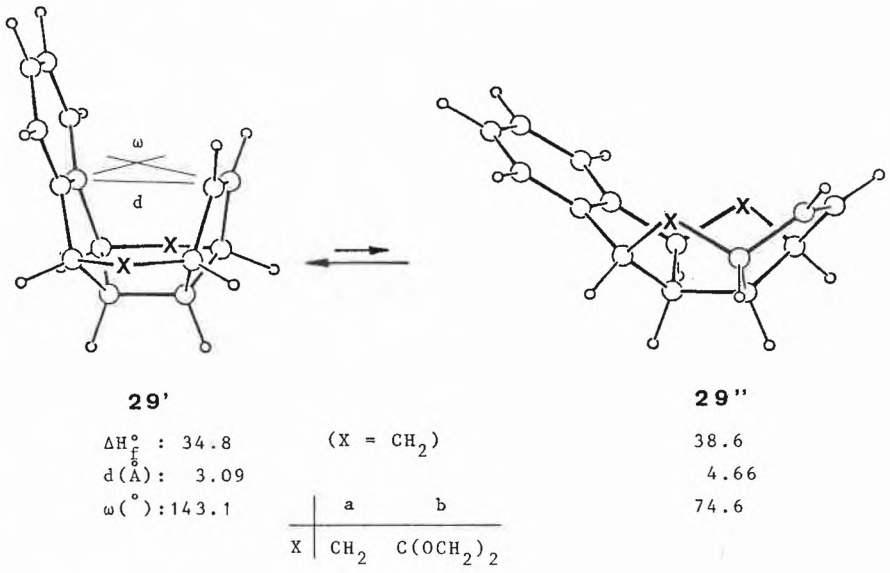
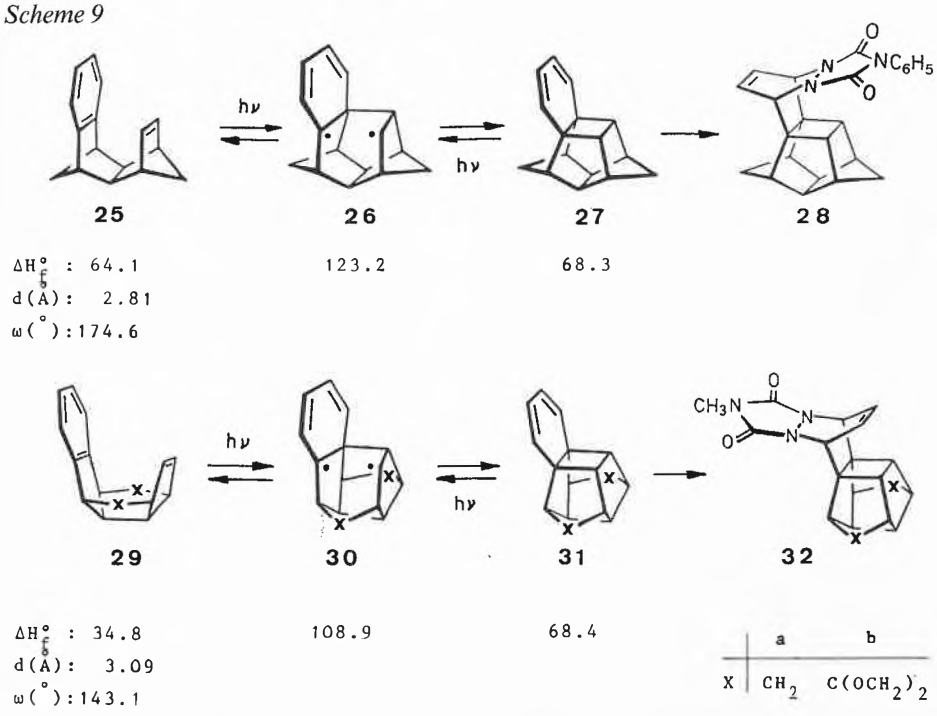
Scheme 6



Scheme 8



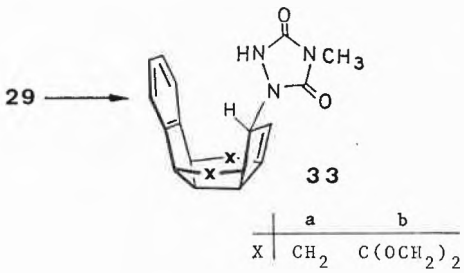
Scheme 9



tion **29'** (Scheme 8) is again predicted. Qualitative experimental indications (for **29a**) in this direction are the vicinal coupling constants of the methylene protons (ca. 8/0 Hz) for **29a** and the diamagnetic shift ($CDCl_3$) of the olefinic H-signal at $\delta = 4.86$ vs. $\delta = 5.29$ for **18a**.

Intramolecular photo-benzo/ene-cycloadditions ([6+2]) are rarely observed[3]. It remains unclear whether the failure is due to photochemical or thermal product instability[17]. One of the few successful intramolecular [6+2]-additions has been achieved in the **A-2** system **25** (Scheme 9), where 254 nm monochromatic or acetone (xanthone) sensitized excitation causes 2:1 and 4:1 (1:3) photoequilibria[22], respectively, with **27**. Cycloadduct **27** was additionally characterized as the *N*-phenyltriazolinedione adduct **28** (at room temperature ca. 98% **28** and 2% of the *endo*-isomer; NOE). Thermally, **27** was stable up to at least 250°C in benzene solution. The E_a value (ca. 57 kcal/mol) for the back reaction to **25** in the vapor phase compares well with the $\Delta\Delta H_f^0$ value of 54.9 kcal/mol for **27/26**. Comparison of the MM2 data for the structures **25–27** with those of the **B-2** series (**29a–31a**) revealed i.a. practically equal ΔH_f^0 values for the isomeric photoadducts **27/31a**. As judged by the $\Delta\Delta H_f^0$ values of **27/31a** and the diradicals **26/30a** (54.9/40.5 kcal/mol), **31a** was expected to be thermally less stable than **27**. This prognosis has been confirmed: sensitized excitation of hydrocarbon **29a** (ca. 10^{-4} M solution, benzene, acetone, xanthone; 0°C) causes very slow conversion and exclusive polymer formation (via **30a**?). Direct irradiation with monochromatic 254 nm light (ca. 10^{-4} M isooctane solution; 0°C) caused no change at all and with polychromatic light of the high pressure Hg lamp (vycor vessel), again only polymerization was observed. Addition of excess *N*-methyltriazolinedione (NMTD) to such photolysis solutions furnished only the ene-adduct[22] **33a** (Scheme 10) of unreacted **29a**[23]. However, on irradiation at −75°C and addition of

Scheme 10

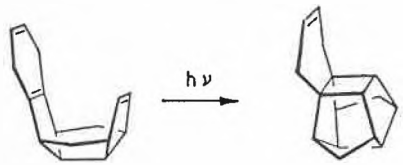


NMTD at this temperature after various irradiation times, up to 5% of the [4+2]-adduct **32a** was identified in addition to **33a**. In the same set of sensitized irradiations, the bisacetal **29b** also furnished only polymers and again proved to be stable towards 254 nm light. Upon polychromatic irradiation and addition of NMTD depending on the temperature (0°C/

–75° C), 6%/25% of the crystalline adduct **32b** (NOE) were formed besides 94%/75% of unreacted **29b** and its ene-adduct **33b**. Since the above given material balance for **29b/33b**: **32b** was practically constant after a minimum of 4 h irradiation, the existence of a photoequilibrium **29b**⇄**31b** is highly probable. The formation of **31b** is further evidenced by the isolation of a 1:1 adduct of the type **32b** when excess dimethyl acetylenedicarboxylate was added to a low temperature photolysis solution. The direct, low temperature identification of photoisomers **31a, b** and a more detailed knowledge of their thermal stability will be needed in order to address the obvious discrepancy with the ΔH_f^0 difference of 40.5 kcal/mol calculated for **31a/30a**.

The photochemistry of **34** (Scheme 11), obtained by Birch reduction of **29a**, was of special interest in connection with the photobehavior of **44**. Not surprisingly, upon sensitized excitation (acetone), [2+2]-addition had to compete with dehydrogenation and resulted in a mixture of 70% **35** and 30% **29a**.

Scheme 11



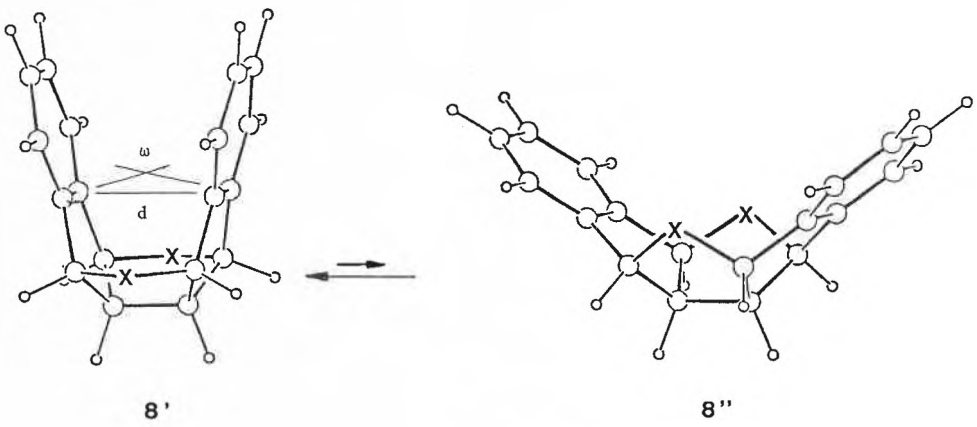
3. *Benzo/Benzo-Cycloadditions (***B-3***)*

The MM2 derived results and ^{1}H-NMR data (i.a. $J_{1,12\alpha} = 7$, $J_{1,12\beta} = 1.5$ Hz) for the **B-3** compound **8a** revealed an increasing energetic advantage of the «closed» conformation **8a′** with *d* and *ω* values very similar to that calculated for **29a′** (Scheme 12). According to the X-ray analysis of both **29a** and **1** the MM2 calculations underestimate the transannular interactions. The experimental *d* value of **8a** is 0.19 Å larger than that of **1** (Scheme 13). As a consequence of the weaker transannular π/π-compression, the pyramidalization found in **1** is missing and the diamagnetic shift of the benzene protons caused by the opposite benzene ring is weaker. The influence of the C-5 and C-12 substitution (bisacetal **8b**, diketone **8c**, bis(dicyanomethylene) compound **8d**) upon potential equilibration **8′** ⇄ **8″** as well as stability of the products **9** was expected to be comparable to that in the non- and mono-anellated analogs **18a–d** and **29a, b**.

All intramolecular benzo/benzo [6+6]-photoadducts which could be isolated up to date, were derived from **A-3** skeletons[1]. As exemplified with **1** (Scheme 13), the nature of the light is crucial. With polychromatic light (high pressure Hg lamp, pyrex or quartz filter), no **2** was observed and irradiation of **2** under these conditions led back to **1**. With monochromatic light of λ = 254 nm (low pressure Hg lamp), a 7:3 equilibrium **1:2** was established, in qualitative agreement with the relative extinction coefficients. The unexpectedly high thermal stability of the «*syn-o,o*-dibenzene» **2**[24] allowed the addition of numerous dienophiles to give the domino Diels-Alder adducts **37**[4]. The experimental $E_a = 37$ kcal/mol for the highly selective b-cleavage to give **1** is ca. 8 kcal/mol greater than the calculated ΔH_f^0 difference for **2/36** and is interpreted in terms of a «forbidden» [σ2+σ2]-cycloreversion.

In close analogy to the situation with the isomeric benzo-ene derived cage compounds **27/31**, practically identical ΔH_f^0 values were calculated for the benzo-benzo photoisomers **2/9a**. Once more, with ΔH_f^0 differences of 29.7 and 20.5 for **2/36** and **9a/38a**, respectively, the stability of the **B**

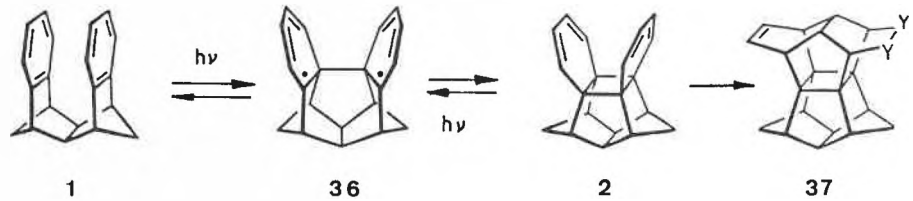
Scheme 12



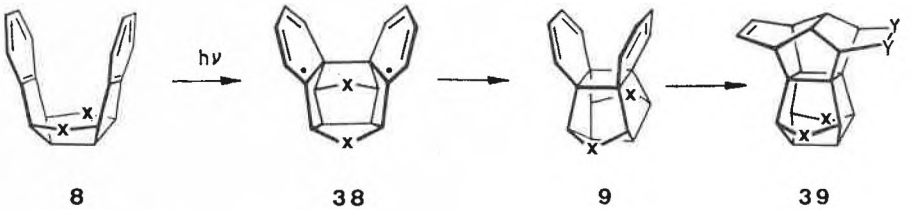
	8′		8″
ΔH_f°	37.7	(X=CH_2)	42.8
d (Å)	3.04		4.64
ω (°)	144.8		74.95

X	a: CH_2	b: $C(OCH_2)_2$	c: C=O	d: $C=C(CN)_2$

Scheme 13



	1		36	2	37
	exp.				
ΔH_f°	65.1		142.0	112.3	
d (Å)	2.86	3.04			
ω (°)	172.5	161.4			



	8		38	9	39
	exp				
ΔH_f°	37.7		133.0	112.5	
d (Å)	3.04	3.23			
ω (°)	144.8	147.4			

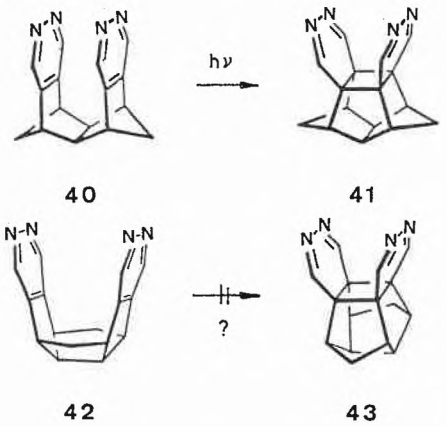
X	a: CH_2	b: $C(OCH_2)_2$	c: C=O	d: $C=C(CN)_2$

isomers **9** should be significantly lower than that of the **A** isomers and substantially lower than that of the monobenzo-derived analogs **31**.

In view of the findings with **29a, b**, it came as no surprise that with **8a–d**, under direct or sensitized excitation conditions as low as −75° C, no indication for the formation of **9a–d** or, after addition of NMTD (at −75°C), of the adducts **39a–d** was found. Matrix irradiation experiments with **8a–d** may furnish more insight.

Irradiation experiments with the isomeric bispyridazines **40** and **42** (Scheme 14) manifested the same structure-dependency. When **40** was exposed to 300 nm light (ca. 10^{-2} M methanol solution; room temperature), only [6+6]-adduct **41** is observed at up to ca. 50% conversion. Prolonged irradiation caused polymerization. Under the same conditions, as well as with 254 nm light, **42** proved to be stable over 24 h.

Scheme 14



40 **41** **42** **43**

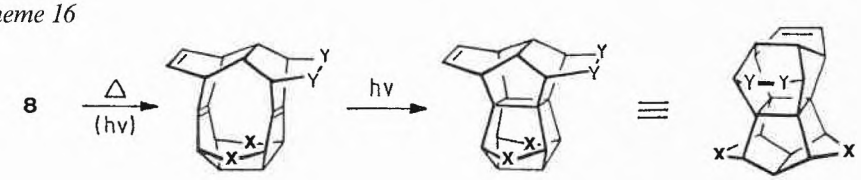
Before the thermal lability of skeleton **9** was recognized as the probable cause for not observing [6+6]-addition in **8**, an alternative way to **9** was seen in the [2+2]-addition of the tetraene **44** (Scheme 15). The latter is easily available from **8a** by twofold Birch reduction. However, under the conditions successfully applied to the [2+2]-addition **34**→**35**, only dehydrogenation to give **8a** occured. The hypothesis that steric interference between the inner pairs of methylene hydrogens of the two cyclohexene units in **45** might be responsible, is to be tested with the mono- and bis-*p*-quinones[25]. Clearly, the [2+2]-cycloadduct(s) **46** derived from the enedione(s) **45** would also feature structural rigidity of the type that is required for long-lived radical cations and dications exemplified by **6**/**13** and **17**/**14**.

Independent of the reasons for not observing the [6+6]-adducts of type **9**, it is obvious that the original preparative goal (Scheme 2) has become highly improbable. Alternative approaches are therefore planned: an attractive one leading to [2.2.1.1]isopagodanes **39** involves the high-pressure domino Diels-Alder addition of an acetylene equivalent to dibenzo-substrates **8** followed by photo-[2+2]-cyclization in **47** (cf. e.g. **20**→**22**) (Scheme 16).

Scheme 15

44 **45** **46**

Scheme 16



47 **39**

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[16] Cf. H. Prinzbach, G. Sedelmeier, H.-D. Martin, *Angew. Chem. Int. Ed. Engl. 16* (1977) 103.
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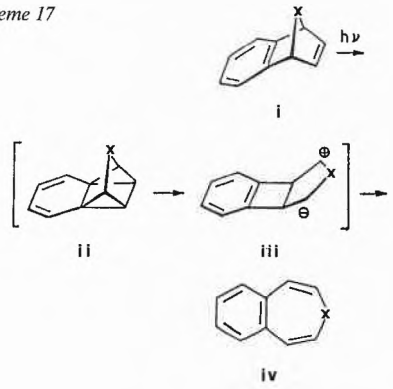
Scheme 17



i **ii** **iii** **iv**

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[25] It has been shown recently, that the bis-*p*-quinone **44** upon prolonged irradiation with a 150 W high-pressure Hg lamp (ca. 10^{-3} M $CHCl_3$ solution, room temperature, durane filter (316 nm)) quantitatively yields the *p*-quinone dimer **46**. The intermediate [2 + 2]-adduct **45** can be isolated from a ca. 4:1 mixture with **46** obtained after ca. 50% conversion.