22. New Heptalenes Substituted with Extended π-Systems

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The synthesis of π-substituted heptalenecarboxylates or -dicarboxylates, starting with the easily available dimethyl 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate (**2b**), are described. Treatment of **2b** with *t*-BuOK and C_2Cl_6 at −78° leads to the chemoselective introduction of a Cl substituent in Me–C(1) (see **5b** in *Scheme 1*). Formation of the corresponding triphenylphosphonium salt **7b** *via* the iodide **6b** (*Scheme 2*) allowed a *Wittig* reaction with cinnamaldehyde in the two-phase system CH_2Cl_2/2N NaOH. Transformation of the 4,5-dicarboxylate of **2b** into the corresponding pseudo-ester **10b** allowed the selective reduction of the carbonyl function at C(4) with DIBAH to yield the corresponding 4-carbaldehyde **11b** (*Scheme 3*). *Wittig* reaction of **11b** with (benzyl)triphenylphosphonium bromide led to the introduction of the 4-phenylbuta-1,3-dienyl substituent at C(4). The combination of both *Wittig* reactions led to the synthesis of the 1,4-bis(4-phenylbuta-1,3-dienyl)-substituted heptalene-5-carboxylate (all-*E*)-**17b** (*Scheme 5*). In a similar manner, by applying a *Horner-Wadsworth-Emmons* reaction, followed by the *Wittig* reaction, the donor-acceptor substituted heptalene-5-carboxylate (*E*;*E*)-**22b** was synthesized (*Scheme 7*). Most of these new heptalenes are in solution, at room temperature, in thermal equilibrium with their double-bond shifted (DBS) isomers. In the case of (all-*E*)-**17b** and (*E*;*E*)-**22b**, irradiation of the thermal equilibrium mixture with light of $\lambda = (439 \pm 10)$ nm led to a strong preponderance (> 90%) of the DBS isomers **17a** and (*E*;*E*)-**22a**, respectively (*Schemes 6* and *7*). Heating of the photo-mixtures at 40° re-established quickly the thermal equilibrium mixtures. Heptalenes-carboxylates (all-*E*)-**17a** and (*E*;*E*)-**22a** which represent the off-state of a 1,4-conjugative switch (CS) system show typical heptalene UV/VIS spectra with a bathochromically shifted heptalene band III and comparably weak heptalene bands II and I which appear only as shoulders (*Figs. 4* and *5*). In contrast, the DBS isomers (all-*E*)-**17b** and (all-*E*)-**22b**, equivalent to the on-state of a 1,4-CS system, exhibit extremely intense heptalene bands I and, possibly, II which appear as a broad absorption band at 440 and 445 nm, respectively, thus indicating that the CSs (all-*E*)-**17a** ⇌ (all-*E*)-**17b** and (*E*;*E*)-**22a** ⇌ (*E*;*E*)-**22b** are perfectly working.

Introduction. – In a preceding communication [1], we have shown that the introduction of π-donor substituents such as (*E*)-styryl, (*E*)-4-methoxystyryl, or 4-methoxyphenyl into heptalene-1,2- and -4,5-dicarboxylates have a marked and distinctly different influence on the two double-bond shifted (DBS) isomers of the heptalenes depending on the fact whether the π-donor substituent is located in 'through-conjugation' to one of the ester groups or not. Since the DBS process in heptalenes can easily be induced thermally or photochemically (see lit. cit. in [1]), heptalenes of the described type may be regarded as conjugative switches (CS), characterized by an 'on-state' with 'through-conjugation' and an 'off-state' where the conjugation is interrupted. An example is shown in *Fig. 1*.

The (*E*)-styryl-substituted heptalene-1,2-dicarboxylate **1a**, which displays in its UV/VIS spectrum (hexane/4% i-PrOH) the heptalene band I (see [1]) as a very weak shoulder at *ca.* 400 nm, followed by the more intense heptalene band II, appearing also

[1]) Part of the planned Ph.D. thesis of *S. E.*, University of Zurich.

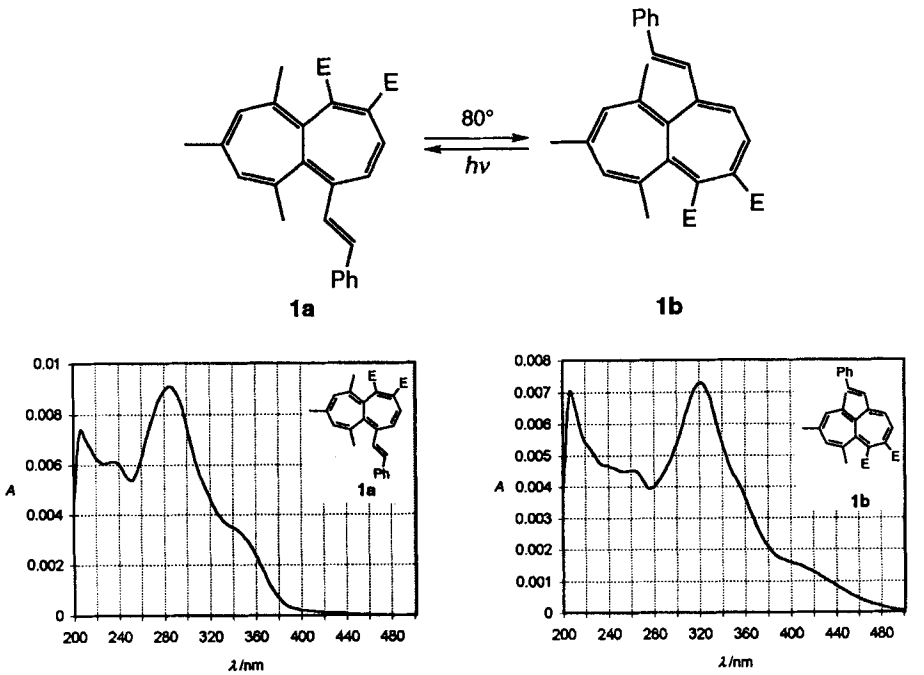


Fig. 1. *Dimethyl 6,8,10-trimethyl-4-[(E)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**1a** and **1b**, resp.), *representing the off-state and the on-state of a conjugative switch* (from [1])

as a shoulder at 345 nm, is acting as the off-state. Heating of **1a** at 80° activates the DBS process which leads to **1b**, equivalent to the on-state. The UV/VIS spectrum of **1b** exhibits, due to the 'through-conjugation' of the (*E*)-styryl group at C(1) and the MeOCO moiety at C(4), markedly enhanced heptalene bands I and II as shoulders at *ca.* 400 and 355 nm, respectively.

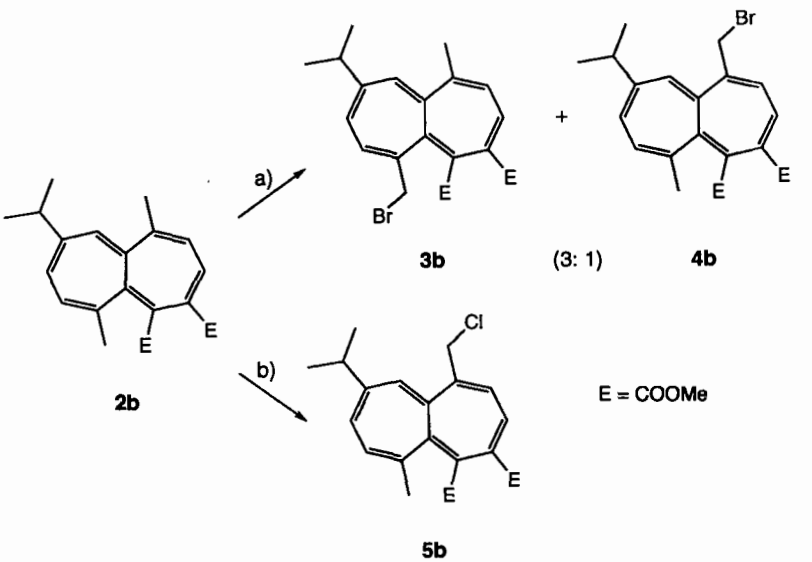
To test the effect of substituents with more extended π-systems at C(2) and C(5), or C(1) and C(4) on the position and intensities of the heptalene bands I to III, we were interested in the construction of such structures.

Results. – Since the formation of heptalene-dicarboxylates such as **1b** by thermal or catalyzed reaction of correspondingly substituted azulenes and dimethyl acetylenedicarboxylate (ADM) [2] was not suitable for our projected heptalenes, we had to develop new synthetic ways for these compounds. Our idea was to start already with heptalene-dicarboxylates, especially with dimethyl 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate (**2b**) which is formed thermally in good yield from commercially available guaiazulene and ADM [3][2]). We assumed that the established 'through-conjugation' in 1-substituted

[2]) We found that, on a 10-g scale, average yields of >65% of **2b** can be obtained, when 7% (by weight) solutions of guaiazulene in toluene are reacted with a three-fold molar amount of ADM at 130°/24 h.

heptalene-4,5-dicarboxylates (*cf.* **1b**) should also be effective chemically, *i.e.*, it should be expressed in a higher acidity of the H-atoms of the Me group at C(1) as compared to that of the H-atoms of the Me group at C(6) in **2b**. Indeed, the reactivity differences of the two Me groups in **2b** are striking. Whereas *N*-bromosuccinimide (NBS) in boiling CCl_4 leads mainly to the introduction of a Br substituent at the 'olefinic' Me group at C(6), the reaction of **2b** with *t*-BuOK in THF at $-78°$ in the presence of C_2Cl_6 as electrophilic chlorinating agent gave exclusively, in excellent yields, the 1-(chloromethyl)heptalene **5b** (*Scheme 1*). The structure of the crystalline **3b** and **5b** was established by ^{1}H-NOE measurements. Irradiation of H–C(10) in **3b** (*s* at 5.85 ppm; $CDCl_3$) induced a strong enhancement of the signal of Me–C(1) at 2.20 ppm, but no effect on the *AB* system of $BrCH_2$–C(6) at 4.25 and 4.03 ppm (J_{gem} = 10.1 Hz). The opposite effects were observed when H–C(10) of **5b** (*s* at 5.90 ppm; $CDCl_3$) was irradiated. In this case, the signals of the *AB* system of $ClCH_2$–C(1) at 4.21 and 4.15 ppm (J_{gem} = 12.2 Hz) were strongly enhanced, in contrast to the signal of Me–C(6) at 2.04 ppm which remained unchanged[3]).

Scheme 1

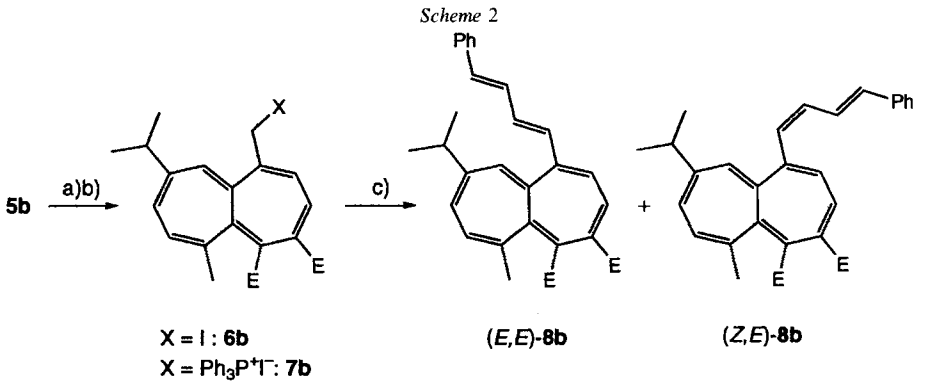


a) NBS in boiling CCl_4 in the presence of catalytic amounts of $(PhCOO)_2$; 76%; bromide **3b** decomposed before melting. b) *t*-BuOK/C_2Cl_6 in THF at $-78°$; 90%; m.p. of **5b**: 109.5–111.0°.

Reaction of **5b** with NaI in acetone gave quantitatively the crystalline, but unstable iodide **6b** (*AB* system of ICH_2–C(1) at 4.18 and 4.04 ppm with J_{gem} = 9.0 Hz). Further reaction of **6b** with Ph_3P in acetone led to the formation of the corresponding phosphonium iodide **7b** (*Scheme 2*). Deprotonation of this salt in the two-phase system CH_2Cl_2/2N

[3]) The ^{1}H-NMR spectrum ($CDCl_3$) of **4b** was almost identical with that of **5b**. The *AB* system of $BrCH_2$–C(1) appeared at 4.13 and 3.95 ppm (J_{gem} = 12.5 Hz). The larger value for J_{gem} for **4b** as compared to **3b** is in agreement with a strong 'through-conjugation' in the latter (*cf.* [4]). None of the halogenated heptalenes **3b**–**6b** displayed in their ^{1}H-NMR spectra signals of the corresponding DBS isomers **3a**–**6a**.

Scheme 2



a) Chloride **5b** in acetone/NaI, room temperature/4 h; > 90% isolated yield; m.p. of **6b**: 146.5–148.2°. b) Iodide **6b** in acetone/PPh_3, room temperature/4 h; > 90% isolated yield. c) CH_2Cl_2/2N NaOH in the presence of 6 mol-equiv. cinnamaldehyde, room temperature/3 d; 51% yield of crystalline (*E,E*)-**8b** and small amounts of crystalline (*Z,E*)-**8b**.

NaOH at room temperature in the presence of cinnamaldehyde resulted in the immediate appearance of a deeply red color which changed after stirring for 3 d at room temperature under Ar into orange as an indication for the completion of the *Wittig* reaction. The formed crystalline 1-(4-phenylbuta-1,3-dienyl)heptalene-dicarboxylate (*E,E*)-**8b** represented the pure (1′*E*,3′*E*)-isomer (m.p. 159.4–161.4°). The small amounts of the (1′*Z*,3′*E*)-isomer (*Z,E*)-**8b** remained in the mother liquors, but could also be isolated in crystallized form (m.p. 112.9–113.7°). The ^{1}H-NMR spectrum ($CDCl_3$) of (*E,E*)-**8b** resembled very much that of the corresponding 1-[(*E*)-styryl] analogue (*cf.* [1][2]) with the exception of the olefinic region which showed two additional coupled H-atoms with H–C(1′) at 6.54 (*d*, J_{vic} = 15.0 Hz), H–C(2′) at 6.39 (*dd*, J_{vic} = 15.0 and 10.5 Hz), H–C(3′) at 6.83 (*dd*, J_{vic} = 15.5 and 10.5 Hz), and H–C(4′) at 6.57 ppm (*d*, J_{vic} = 15.5 Hz). Compound (*Z,E*)-**8b** exhibited the signals of the butadienyl side chain at 6.97 ($CDCl_3$; *dd*, J_{vic} = 15.3 and 11.3 Hz; H–C(3′)), 6.52 (*d*, J_{vic} = 15.3 Hz; H–C(4′)), 6.17 (*t*-like, $\sum J_{vic}$ = 23.3 Hz; H–C(2′)), and 6.08 ppm (*d*, J_{vic} = 12.0 Hz; H–C(1′)).

Irradiation of (*E,E*)-**8b** with light of $\lambda = (439 \pm 10)$ nm (interference filter; *Schott Schleiffer AG*) at 10° in hexane solution did not lead to the formation of the DBS isomer (*E,E*)-**8a** in detectable amounts (HPLC).

The UV/VIS spectrum of (*E,E*)-**8b** resembles, as expected, very much that of the corresponding 1-[(*E*)-styryl]heptalene **9b** (*cf. Fig. 2* and *Table*) [1]; however, (*E,E*)-**8b** exhibits much stronger shoulders for the heptalene bands I and II at *ca.* 410 and 369 nm, respectively. The heptalene band III of **8b** is bathochromically shifted by 16 nm as compared to the heptalene band III of **9b**.

For the introduction of the 4-phenylbuta-1,3-dienyl group at C(4), we had to transform the MeOCO–C(4) moiety in **2b** chemoselectively either into a CH_2OH group or a CHO function in order to proceed again with a *Wittig* reaction. Since a CH_2OH group at C(4) would lead with the MeOCO–C(5) moiety to the formation of a lactone (*cf.* [5]), we first investigated the selective transformation of the MeOCO–C(4) moiety into a CHO function. More than ten years ago, we described the formation of ortho-anhydrides (pseudo-esters) from heptalene-4,5-dicarboxylates by selective saponification of the ester group at C(4), followed by cyclization to the pseudo-esters under *Stadler* conditions

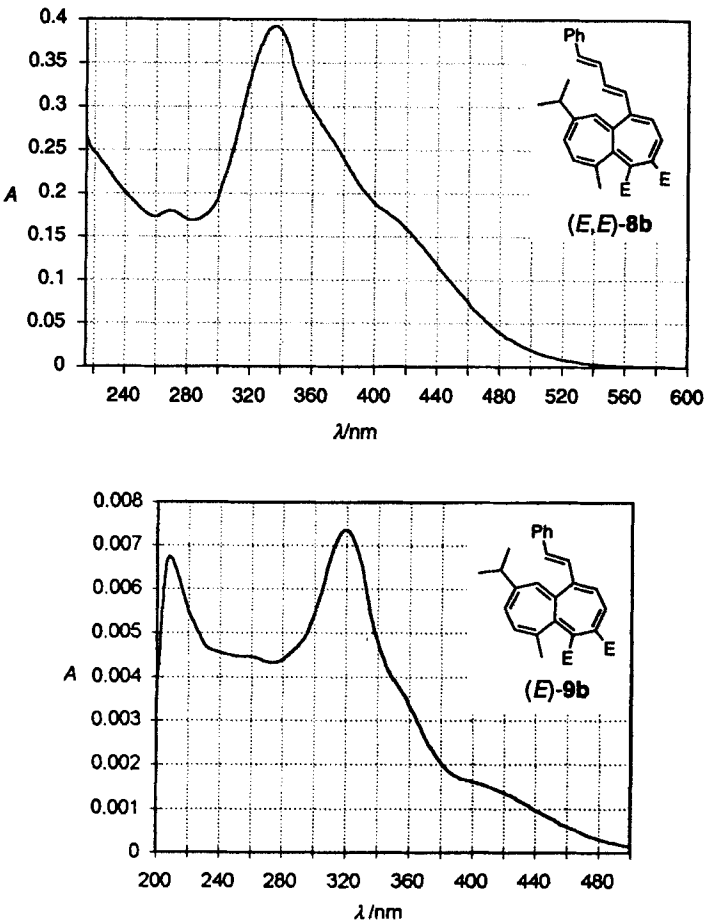


Fig. 2. *UV/VIS Spectra* (hexane/4% i-PrOH) *of* **8b** *and* **9b**[a])

[a]) The spectrum of **9b** was taken from [1]. This and all the other UV/VIS spectra were registered under the same conditions with the photodiode-array detector (wavelength accuracy ±1.5 nm) of an HPLC system from *Waters* (model *911*). For details, see [1].

(see [6]). By this procedure, the pseudo-ester **10b**, which contains now the MeOCO–C(5) moiety protected as an ortho-ester, had already been synthesized (*Scheme 3*) [6b]. Controlled reduction of **10b** with DIBAH in THF at −78° gave a *ca.* 3:1 mixture of the expected carbaldehyde **11b** and the known heptaleno[1,2-*c*]furan-1-one **12b** [5]. This mixture could not be separated chromatographically. However, the furanone did not hinder the following *Wittig* reaction, and, on the other hand, in later experiments (*cf. Scheme 7*) we found that the reduction of **10b** and other pseudo-esters of this type with DIBAH in toluene at −78° occurs cleanly and in over 80% yield without the formation of furanones.

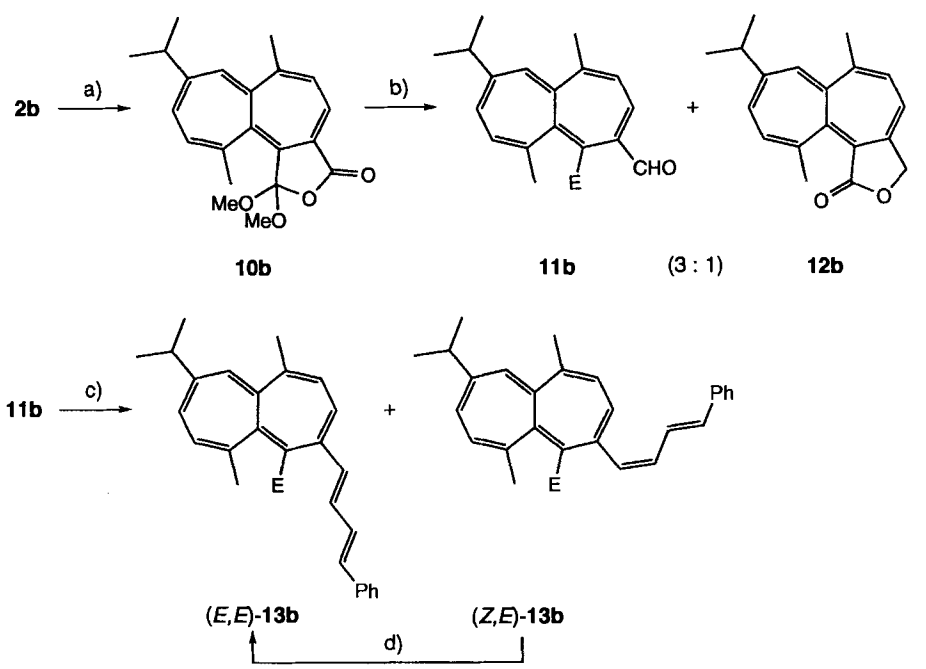
Table. *UV/VIS Spectra of the Heptalene-carboxylates*

Heptalene	λ_{max} [nm][a])			
	I	II	III	IV
(*E,E*)-**8b**	*ca.* 400 (sh, 0.47)	*ca.* 360 (sh, 0.66)	335 (1.00)	270 (0.46)
(*E,E*)-**13a**	*ca.* 430 (sh, 0.03)	*ca.* 350 (sh, 0.92)	335 (1.00)	*ca.* 285 (sh, 0.51)
(*E,E*)-**13b**	*ca.* 445 (sh, 0.04)	*ca.* 330 (< 1)	330 (1.00)	270 (0.53)
(*Z,E*)-**13a**	*ca.* 420 (sh, 0.05)	*ca.* 320 (< 1)	320 (1.00)	285 (1.05)
(*Z,E*)-**13b**	*ca.* 430 (sh, 0.04)	*ca.* 325 (< 1)	325 (1.00)	270 (1.01)
(all-*E*)-**17a**	*ca.* 430 (sh, 0.04)	*ca.* 375 (sh, 0.66)	345 (1.00)	*ca.* 295 (sh, 0.38)
(all-*E*)-**17b**	440 (0.88)	*ca.* 440 (< 1)	360 (1.00)	*ca.* 330 (sh, 0.66)
(*E;E*)-**22a**	*ca.* 440 (sh, 0.04)	*ca.* 350 (sh, 0.84)	340 (1.00)	*ca.* 320 (sh, 0.87)
(*E;E*)-**22b**	445 (1.15)	*ca.* 445 (< 1)	375 (1.00)	*ca.* 345 (sh, 0.87)

[a]) In parentheses are given the relative intensities.

The reaction of the mixture **11b**/**12b** with (cinnamyl)triphenylphosphonium bromide in the two-phase system CH_2Cl_2/2N NaOH at room temperature led to a mixture of (*E,E*)-**13b** and its (1′*Z*)-isomer (*Z,E*)-**13b**. Moreover, the reaction mixture contained

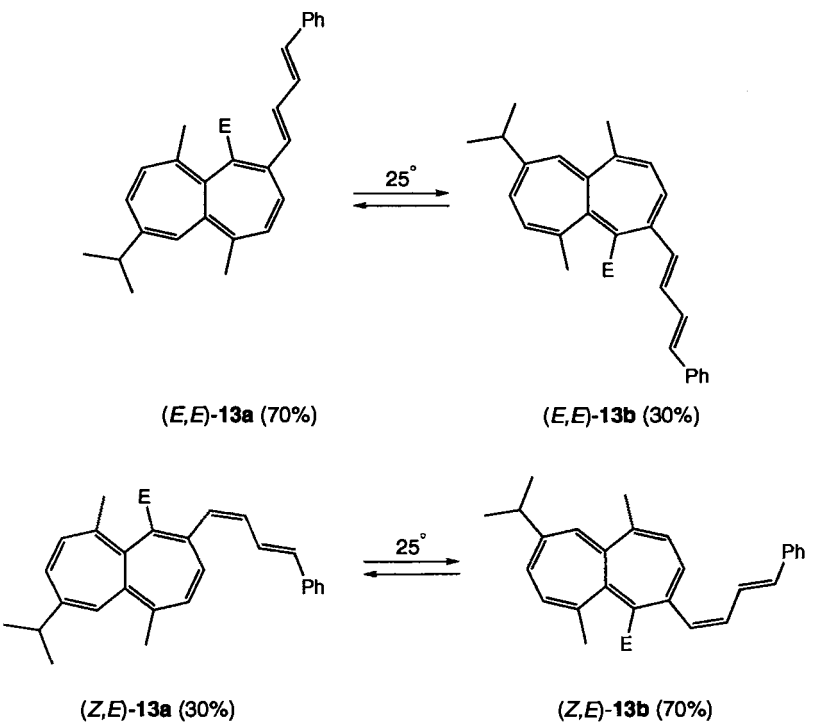
Scheme 3



a) 1. KOH in $EtOH/H_2O$, 20–40°. 2. $DMF/(COCl)_2$, MeCN, 0°; MeOH; 63% [6b]. At room temperature, in $CDCl_3$ solution, **10b** is with (1.3±0.3)% of its DBS isomer **10a** in thermal equilibrium [6b]. b) 3–5 mol-equiv. DIBAH in THF, −78°/2 h; 80%. The 3:1 mixture of **11b** and **12b** [5] represented a yellow oil. c) Mixture of **11b**/**12b** and (cinnamyl)triphenylphosphonium bromide in CH_2Cl_2/2N NaOH, room temperature/2 h; 31% of a mixture of (*E,E*)-**13b** and (*Z,E*)-**13b** and their DBS isomers (*E,E*)-**13a** and (*Z,E*)-**13a** (see text). d) Catalytic amount of I_2 in hexane/Et_2O (1:1), room temperature/6 h.

also, in thermal equilibrium, the corresponding two DBS isomers (*E,E*)-**13a** and (*Z,E*)-**13a** (^{1}H-NMR and HPLC evidence). Chromatography on silica gel (hexane/Et_2O 7:1) allowed the separation of (*E,E*)-**13a** and (*Z,E*)-**13b**. Both forms underwent isomerization readily at room temperature to yield the corresponding thermal equilibrium mixtures of (*E,E*)-**13a** and (*E,E*)-**13b** (70:30) as well as of (*Z,E*)-**13a** and (*Z,E*)-**13b** (30:70; *cf. Scheme 4*). Treatment of the mixture of (*Z,E*)-**13a**/(*Z,E*)-**13b** with a catalytic amount of I_2 in hexane/Et_2O (1:) at room temperature led exclusively to the mixture (*E,E*)-**13a**/(*E,E*)-**13b**[4]). The UV/VIS spectra of **13a** and **13b** are shown in *Fig. 3*. The two DBS forms represent the on-state ((*E,E*)-**13a**) and the off-state ((*E,E*)-**13b**) of a 1,2-CS system (*cf.* [1]). The spectrum of (*E,E*)-**13a** is characterized by a weak heptalene band I which appears as a just recognizable shoulder at *ca.* 430 nm (see also the *Table*). The heptalene band II is strongly enhanced in comparison to other heptalene-1,2-dicarboxylates (*cf.* [1]), but also only visible as a shoulder at *ca.* 350 nm sitting on the long-wavelength flank

Scheme 4



[4]) The described isomerizations could easily be followed by ^{1}H-NMR spectroscopy, since all four isomers showed *inter alia* different chemical shifts ($CDCl_3$) for their MeOCO groups: 3.69 ((*E,E*)-**13b**), 3.63 ((*E,E*)-**13a**), 3.60 ((*Z,E*)-**13a**), and 3.54 ppm ((*Z,E*)-**13b**). The (1′*E*,3′*E*)-configuration of the 4-phenylbutadienyl side chain of (*E,E*)-**13a** is indicated by the corresponding vicinal coupling constants in the ^{1}H-NMR spectrum ($CDCl_3$): 7.64 (*d*, J_{vic} = 15.4 Hz; H–C(4′)), 6.98 (*dd*, J_{vic} = 15.5 and 10.5 Hz; H–C(2′)), 6.77 (*dd*, J_{vic} = 15.5 and 10.7 Hz; H–C(3′)), and 6.69 (*d*, J_{vic} = 15.5 Hz; H–C(1′)). The position of the C=C bonds at the heptalene perimeter is signified by the *AB* systems of H–C(3) and H–C(4) as well as of H–C(8) and H–C(9) with J_{AB} = 12 Hz.

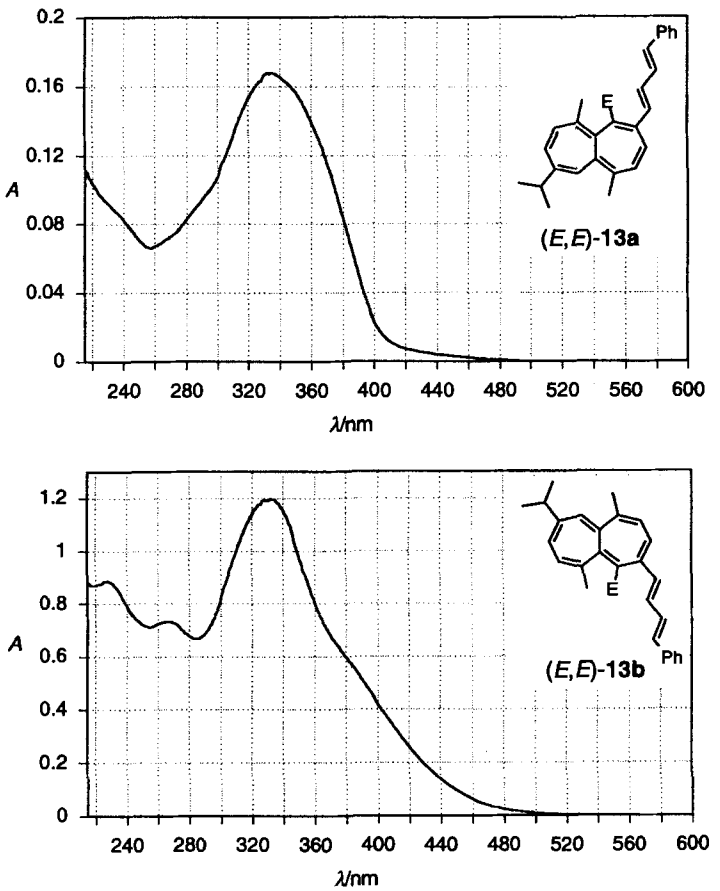


Fig. 3. *UV/VIS Spectra* (hexane/4% i-PrOH) *of* (E,E)-**13a** *and* (E,E)-**13b**

of the heptalene band III at 335 nm. The switch of the π-system in **13b** is clearly testified by the UV/VIS spectrum of this compound. However, the change in the habitus of the spectrum is not very spectacular. The heptalene band III is much slimmer than in (*E*,*E*)-**13a**, since the intensity of band II is markedly reduced. Moreover, band II and band I of **13b** are not well developed, and their position cannot be clearly determined, most probably due to the fact that the intensities of band I and II are quite similar[5]).

The procedures so far described could also be applied to the synthesis of more extended, switchable π-systems as represented by the heptalenes (all-*E*)-**17a** and (all-*E*)-**17b** (*Scheme 5*)[6]). Saponification of the diester **8b** with LiOH in MeOH/H_2O at reflux temperature gave selectively the corresponding mono-acid of **8b** which was transformed

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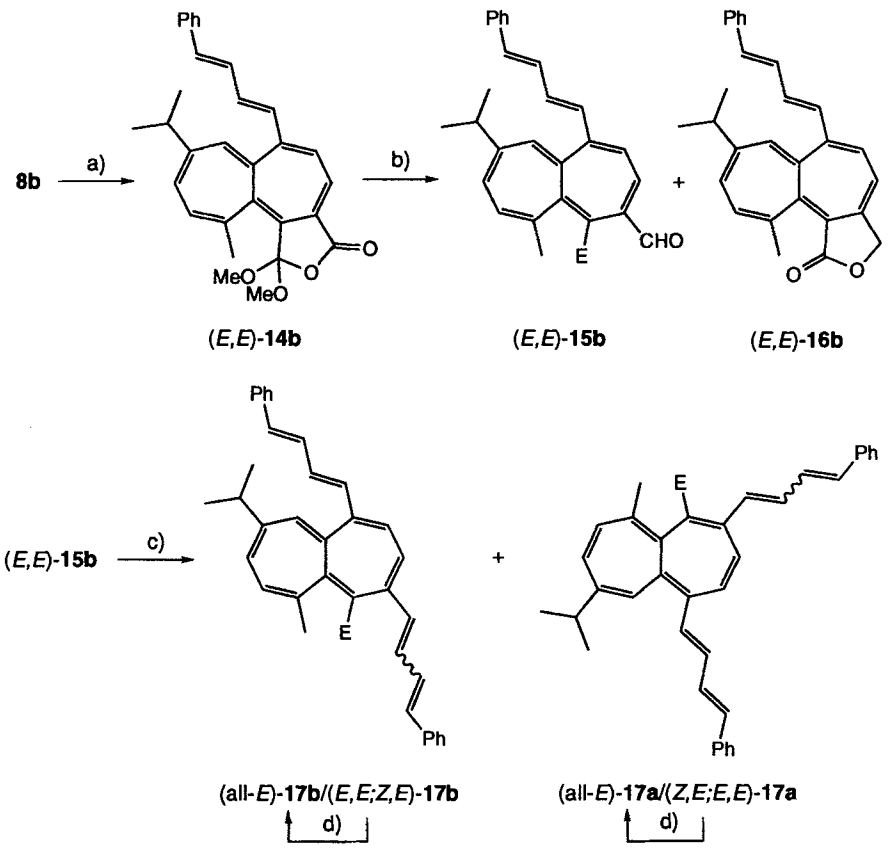
[5]) The two (1′*Z*)-configured heptalenes (*Z*,*E*)-**13a** and (*Z*,*E*)-**13b** show similar effects in the UV/VIS spectra, but less well assignable due to the present (1′*Z*)-configuration.

[6]) We have already reported briefly on the synthesis of (all-*E*)-**17a** and (all-*E*)-**17b** [7]. The UV/VIS for (all-*E*)-**17b** reported there was unfortunately mixed up with that of the isomer of (all-*E*)-**17b** carrying a (1*Z*,3*E*)-buta-1,3-dienyl side chain at C(4).

Scheme 5



a) 1. LiOH, MeOH/H_2O (87:13), reflux/1.5 h. 2. DMF/$(COCl)_2$, MeCN, 0°; MeOH; 81%; m.p. 180.2–180.7°. At room temperature, in $CDCl_3$ solution, *ca.* 1% of the DBS isomer (*E,E*)-**14a** is recognizable in the ^{1}H-NMR spectrum. b) 3 mol-equiv. DIBAH in THF, −78°/1 h; 30% of (*E,E*)-**15b** and 64% of (*E,E*)-**16b**; m.p. of (*E,E*)-**15b**: 138.4–140.0°; m.p. of (*E,E*)-**16b**: 182.1–183.2°. The formyl-ester (*E,E*)-**15b** showed at room temperature in $CDCl_3$ solution no tendency to isomerize to its DBS isomer (*E,E*)-**15a**. On the other hand, lactone (*E,E*)-**16b** was in $CDCl_3$ solution at room temperature in thermal equilibrium with 74% of its DBS isomer (*E,E*)-**16a**. c) Formyl-ester (*E,E*)-**15b** and (cinnamyl)triphenylphosphonium bromide in CH_2Cl_2/2N NaOH, room temperature/2 h; 50%. A 1:0.37:0.07:0.07 mixture of (*E,E*;*Z,E*)-**17b**, (all-*E*)-**17b**, (all-*E*)-**17a**, and (*Z,E*;*E,E*)-**17a**, respectively, was formed. d) Catalytic amounts of I_2 in hexane/Et_2O (1:1), room temperature/6 6

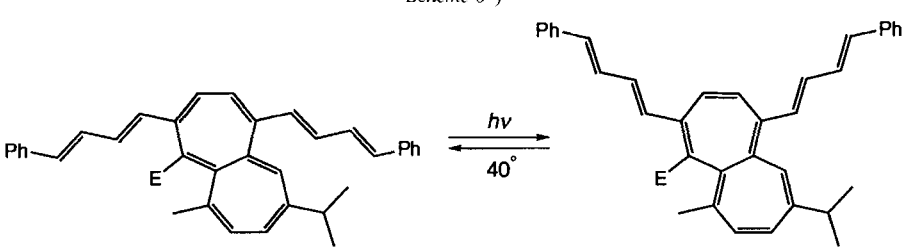
into the pseudo-ester (*E,E*)-**14b** under the usual *Stadler* conditions. The reduction of (*E,E*)-**14b** with DIBAH in THF at −78° led to the formation of the expected formyl-ester (*E,E*)-**15b** in 30% yield. Main product of the reduction was, however, the lactone (*E,E*)-**16b** (64%). In this case, the two products could be separated on silica gel with hexane/Et_2O (7:1). Whereas crystalline (*E,E*)-**15b** showed in solution in the ^{1}H-NMR spectrum ($CDCl_3$) no detectable amount of its DBS isomer (*E,E*)-**15a**, the also crystalline lactone (*E,E*)-**16b** was accompanied in solution by 74% of its DBS isomer (*E,E*)-**16a**. The *Wittig* reaction of the pure (*E,E*)-**15b** with (cinnamyl)triphenylphosphonium bromide in CH_2Cl_2/2N NaOH resulted in the formation of all four possi-

ble products, namely (all-*E*)-**17a** and its DBS isomer (all-*E*)-**17b** as well as (*Z*,*E*;*E*,*E*)-**17a** and its DBS isomer (*Z*,*E*;*E*,*E*)-**17b** with a strong preponderance of (*Z*,*E*;*E*,*E*)-**17b** and (all-*E*)-**17b**. When the solution of all four isomers in hexane/Et_2O (1:1) was stirred in the presence of a catalytic amount of I_2, the two (*Z*,*E*;*E*,*E*)-compounds were almost quantitatively transformed into (all-*E*)-**17b** and (all-*E*)-**17a**. Their thermal equilibrium mixture at room temperature consisted of 78% of (all-*E*)-**17b** and 22% of (all-*E*)-**17a** (*Scheme 6*). On the other hand, when this equilibrium mixture was irradiated with light of $\lambda = (439 \pm 10)$ nm, the amount of (all-*E*)-**17b** could be reduced to $< 10\%$ by a concomitant increase of (all-*E*)-**17a** to $> 90\%$. Heating of this photo-mixture at 40° re-established after 15 min the thermal equilibrium mixture.

The UV/VIS spectra of (all-*E*)-**17a**, respresenting the off-state of this 1,4-CS system (*cf.* [1]), and (all-*E*)-**17b**, equivalent with the on-state, are shown in *Fig. 4*. The three main heptalene bands are clearly recognizable in the spectrum of (all-*E*)-**17a** (see also the *Table*). Band I appears as a weak shoulder at *ca.* 430 nm, followed by the much more intense shoulder of the band II at *ca.* 375 nm which is just recognizable at the long-wavelength flank of band III. The latter one, appearing at 345 nm, represents the dominating absorption band in the spectrum of (all-*E*)-**17a**. The switch to the on-state is very impressive. The spectrum of (all-*E*)-**17b** shows now an immense absorption band at 440 nm, perhaps due to the superposition of the heptalene bands I and II[7]). The heptalene band III is clearly separated and appears at 360 nm, *i.e.*, bathochromically shifted by 15 nm as compared to the off-state spectrum.

The two states of the 1,4-CS system (all-*E*)-**17a** ⇌ (all-*E*)-**17b** can also be recognized by the naked eye. When an orange-colored hexane solution of the thermal equilibrium mixture (all-*E*)-**17a**/(all-*E*)-**17b** is irradiated at *ca.* 0° with (439 ± 10)-nm light in a cuvette and kept in the dark in a second cuvette, only the solution in the irradiated cuvette has turned to pure yellow, clearly distinguishable from the still orange color of the protected solution.

Scheme 6[a])



(all-*E*)-17b **(all-*E*)-17a**

[a]) In hexane solution with $\lambda = (439 \pm 10)$ nm.

[7]) It might be that the strong absorption at 440 nm represents only heptalene band I. In this case, the slight asymmetric absorption band at 360 nm would be constituted of heptalene bands II and III with band II as a weak shoulder sitting on the long-wavelength flank of band III. A final decision can only be made by calculations [8].

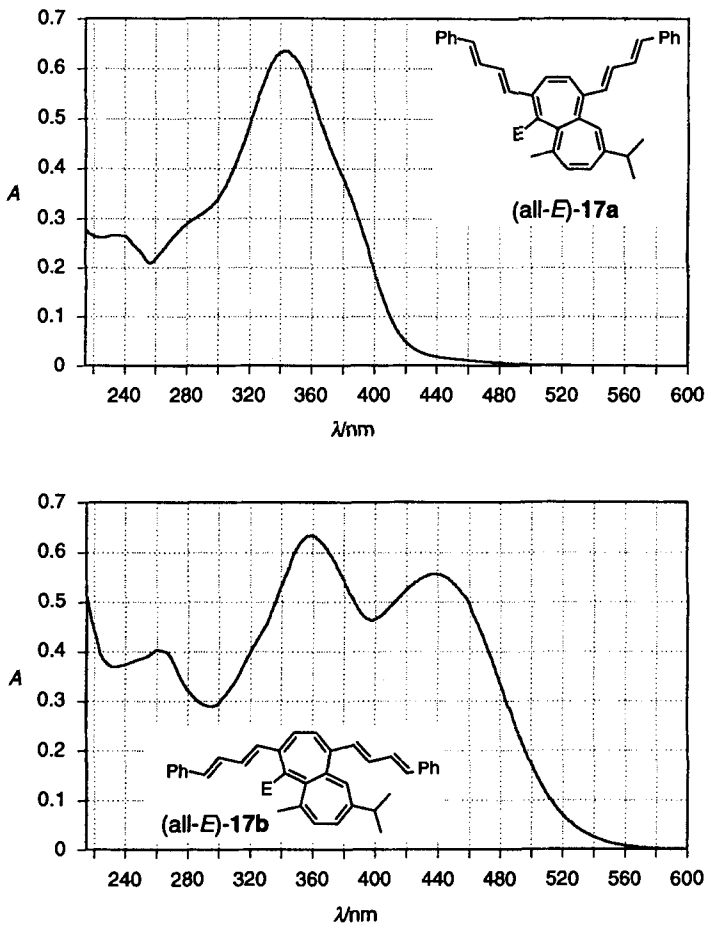
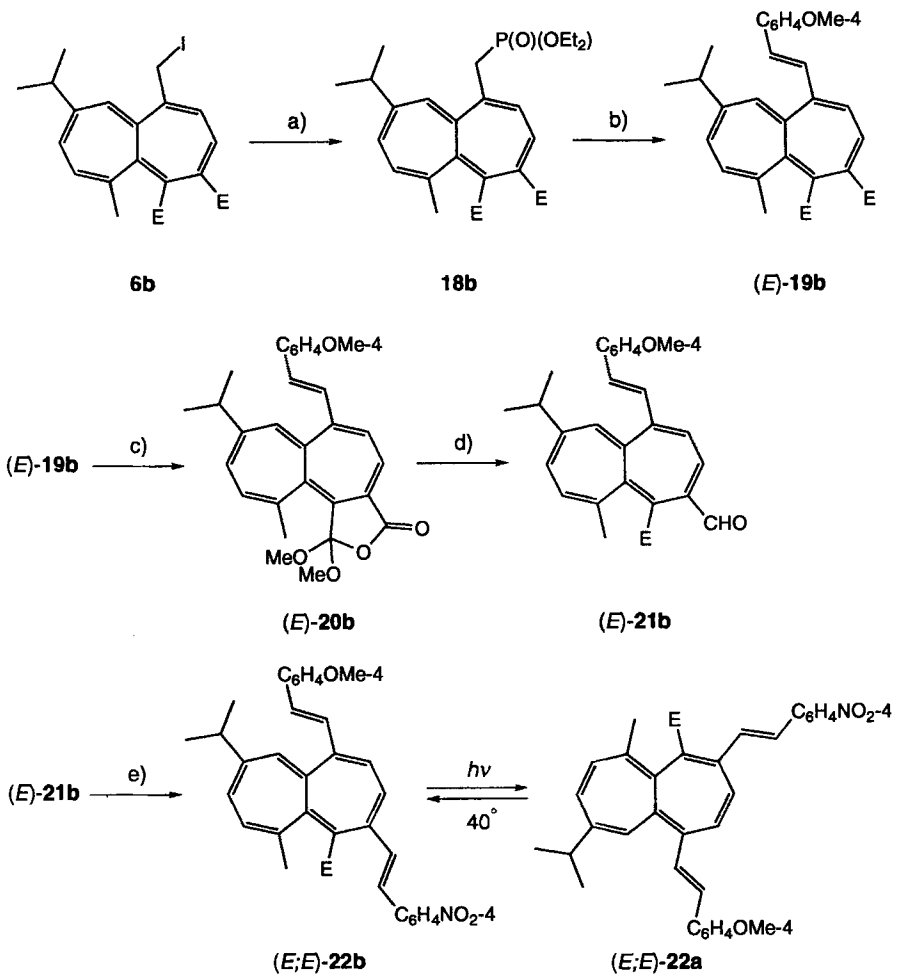


Fig. 4. *UV/VIS Spectra* (hexane/4% i-PrOH) *of (all-*E*)-***17a** *and (all-*E*)-***17b**

To answer the question how the heptalene bands I and II are influenced by strong donor-acceptor substituents in 1,4 relation at the heptalene core, we investigated the heptalene-carboxylate (*E*;*E*)-**22b** carrying an (*E*)-4-methoxystyryl group at C(1) and an (*E*)-4-nitrostyryl moiety at C(4). The procedure for the synthesis of (*E*;*E*)-**22b** is shown in *Scheme 7*.

Since the *Wittig* reaction of the phosphonium iodide **7b** (*cf. Scheme 2*) with 4-methoxybenzaldehyde gave [(*E*)-4-methoxystyryl]-substituted heptalene-dicarboxylate (*E*)-**19b** (see also [2]) in only 20% yield, we applied the *Horner-Wadsworth-Emmons* variant of the *Wittig* reaction for its synthesis which led with sodium bis(trimethylsilyl)amide (NaHMDSA) as base to the pure product in 70% yield. The transformation of (*E*)-**19b** into the corresponding pseudo-ester (*E*)-**20b** could be performed without problems. The reduction of (*E*)-**20b** with 1 mol-equiv. of DIBAH in toluene at −78° proceeded much better than in THF. The pure formyl-ester (*E*)-**21b** was isolated in 80% yield. Only traces of the starting material (*E*)-**20b** and the corresponding furanone could

Scheme 7



a) Excess of $P(OEt)_3$, 90°/40 kPa, 40 min (*cf.* [9]). Phosphonate **18b** was not purified. b) 1.2 Mol-equiv. NaHMDSA/THF. −78°/1 h, 6 mol-equiv. 4-methoxybenzaldehyde, −78 to 20°/15 h; 70%. Only the (*E*)-isomer was formed (*cf.* [2]). c) 1. LiOH, $MeOH/H_2O$ (88:12), reflux/1.6 h. 2. $DMF/(COCl)_2$, MeCN, 0°; MeOH; 62%; m.p. 150.2–151.0°. In $CDCl_3$ solution, at room temperature, *ca.* 1% of the DBS isomer (*E*)-**20a** is present (^{1}H-NMR evidence). d) 1 Mol-equiv. DIBAH in toluene, −78°/15 min; 80%, m.p. 172.9–174.9°. The DBS isomer (*E*)-**21a** could not be found in solution at room temperature (^{1}H-NMR measurement). e) (4-Nitrobenzyl)triphenylphosphonium bromide in CH_2Cl_2/2N NaOH, room temperature/5 h; 3%. In solution, at room temperature, (*E*;*E*)-**22b** was in thermal equilibrium with 14% of its DBS isomer (*E*;*E*)-**22a** ($CDCl_3$; ^{1}H-NMR). Irradiation of this mixture in hexane with light of $\lambda = (439 \pm 10)$ nm (interference filter) shifted the composition to > 90% of (*E*;*E*)-**22a** and < 10% of (*E*;*E*)-**22b**. Heating of this solution at 40° re-established the original thermal equilibrium amounts of 86% of (*E*;*E*)-**22b** and 14% of (*E*;*E*)-**22a**.

be detected by TLC in the original reaction mixture. The *Wittig* reaction of (*E*)-**21b** with (4-nitrobenzyl)triphenylphosphonium bromide in the usual two-phase system led to the formation of a number of side-products which complicated the chromatographic isolation and purification (*E*;*E*)-**22b**. Therefore, the yield of pure (*E*;*E*)-**22b** amounted only to 3% after chromatographic workup. Heptalene (*E*;*E*)-**22b** is a solid which does not crystallize very well. In $CDCl_3$ solution, at room temperature, it is in thermal equilibrium with 14% of its DBS isomer (*E*;*E*)-**22a** (*cf. Scheme 7*). The irradiation of this thermal equilibrium mixture in hexane solution with light of $\lambda = (439 \pm 10)$ nm converts (*E*;*E*)-**22b** to >90% into (*E*;*E*)-**22a**. On the other hand, heating of the hexane solution at 40° for 15 min led readily back to the original thermal equilibrium mixture.

The UV/VIS spectra of (*E*;*E*)-**22a** and (*E*;*E*)-**22b** are shown in *Fig. 5*. The habitus of the spectrum of (*E*;*E*)-**22a** resembles very much that of (all-*E*)-**17a** (*cf. Fig. 4*). However, the main absorption band of (*E*,*E*)-**22a** at 340 nm is appreciably broader than that of (all-*E*)-**17a** at 345 nm. This is chiefly due to the fact that the heptalene band II of (*E*;*E*)-**22a** is much more intense than that of (all-*E*)-**17a**. Also the heptalene band I

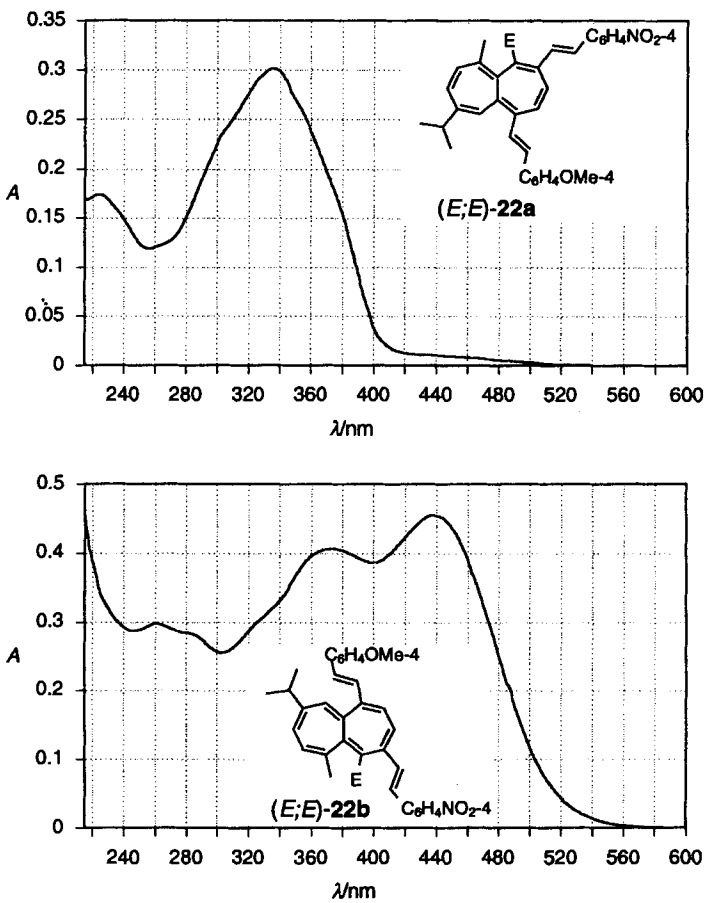


Fig. 5. *UV/VIS Spectra* (hexane/4% i-PrOH) *of* (E;E)-**22a** *and* (E;E)-**22b**

of (*E*;*E*)-**22a** at *ca.* 440 nm seems to be more intense than that of (all-*E*)-**17a**. Moreover, an additional absorption band is recognizable in (*E*;*E*)-**22a** sitting as a shoulder on the low-wavelength flank of the heptalene band III. A comparable band of (all-*E*)-**17a** at 280 nm is much less intense. The switch of the π-bonds in (*E*;*E*)-**22a** induces again a tremendous change in the UV/VIS spectrum of the new heptalene (*E*;*E*)-**22b**. The most intense band appears now at 445 nm. It must have its origin in the heptalene band I and, possibly, II (*vide supra*). The strong absorption at 375 nm (360 nm for (all-*E*)-**17b**) can be assigned to the heptalene band III, followed by a shoulder at the low-wavelength flank at *ca.* 330 nm which may correlate with the shoulder at *ca.* 300 nm of (*E*;*E*)-**22a**.

In conclusion, we can say that the absorption difference of both 1,4-CS systems, *i.e.*, (all-*E*)-**17a** $\rightleftharpoons$ (all-*E*)-**17b** and (*E*;*E*)-**22a** $\rightleftharpoons$ (*E*;*E*)-**22b** for their longest-wavelength bands at 440 and 445 nm, respectively, is with 0.03:1 approximately the same. These pronounced absorption differences are already easily noticeable in diluted solutions with the naked eye. A full paper of this preliminary report will follow in this journal.

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