New Syntheses of Di-π-Substituted Heptalenes

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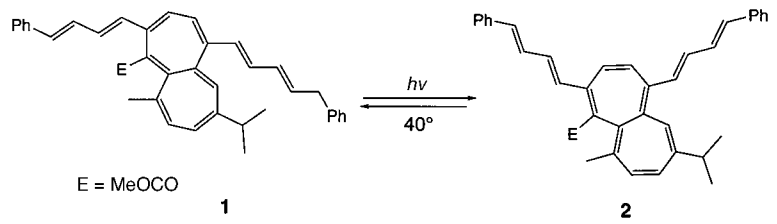
To study the effect of double-bond shifts (DBS) in different type of heptalenes linked to extended π-systems, several di-π-substituted heptalenes were synthesized. 6-[(*E*)-Styryl]heptalene-dicarboxylate **4** was smoothly converted to 1-(chloromethyl)heptalene-dicarboxylate **5** by treatment with *t*-BuOK and C_2Cl_6 in THF at $-78°$. The one-pot reaction of **5** and $P(OEt)_3$ in the presence of NaI, followed by *Wittig-Horner* reaction, afforded the 1,6-di-π-substituted heptalene **6**. The reaction of 6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]heptalenes **7** or **15** with *t*-BuOK and benzaldehyde in THF led to the formation of the 1,6-di-π-substituted heptalenes **13** or **16**, together with transesterification products **14** or **17**. The transformation of the MeOCO group at C(4) of 6-[(*E*)-styryl]heptalene-dicarboxylate **4** to a phenylbuta-1,3-dienyl substituent afforded the 4,6-di-π-substituted heptalene **21a**, which is in thermal equilibrium with its DBS isomer **21b** in solution. Oxidation of heptalene **22** with SeO_2 in dioxane gave carbaldehyde **23**, which was then subjected to a *Wittig* reaction to give the 6,9-di-π-substituted heptalene-dicarboxylate **24**.

1. Introduction. – We have recently shown that two π-substituents at appropriate positions of the heptalene skeleton lead to an enhanced electronic interaction between the two π-substituents *via* buta-1,3-diene subunits of the heptalene π-skeleton (*cf.* heptalene **1**) [1] [2]. This enhanced π-interaction of the substituents with the heptalene core can be destroyed on thermal or photochemical double-bond shift (DBS) to the corresponding not fully conjugated heptalene isomer **2**. These interconversions correspond to a negative thermo- or photochromism, which is positive for the reverse reaction from **2** to **1** (*Scheme 1*).

Scheme 1

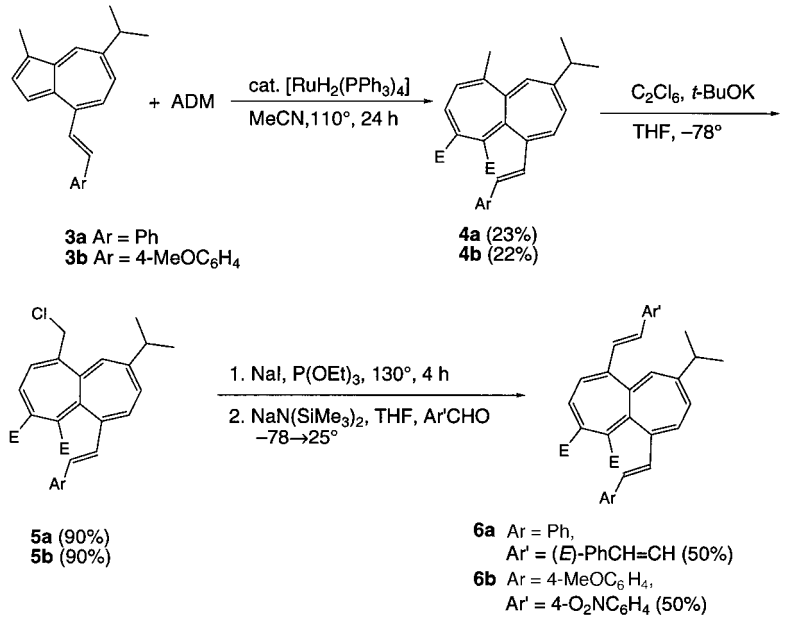


To investigate this enhanced π-interaction of substituents in different types of di-π-substituted heptalenes, we developed the synthesis of such heptalenes.

2. Results and Discussion. – 2.1. *1,6-Di-π-Substituted Heptalenes.* 2.1.1. *With an i-Pr Group at C(9)*. The reaction of easily available 4-styrylazulenes **3a** or **3b** [3] with ADM in the presence of catalytic amounts of $[RuH_2(PPh_3)_4]$ in MeCN at 110° represents the shortest pathway to the 6-styrylheptalene-dicarboxylates **4a** or **4b** in reasonable yields

[4] (*Scheme 2*). The construction of a second π-substituent from Me–C(1) of **4** was achieved according to the protocol that was established earlier in our group [2]. The reaction of **4a** or **4b** with *t*-BuOK in THF at $-78°$ in the presence of C_2Cl_6 as electrophilic chlorinating agent gave, in excellent yield, the 1-(chloromethyl)heptalene-dicarboxylates **5a** or **5b**. The one-pot reaction of **5a** or **5b**, and $P(OEt)_3$ in the presence of NaI at 130° for 4 h, followed by *Wittig-Horner* reaction, afforded 1,6-di-π-substituted heptalene-dicarboxylates **6a** or **6b** in good yield. Unfortunately, compounds **6a** or **6b** showed no detectable DBS to the other isomer on heating or on irradiation at room temperature. The UV/VIS spectra of **6a** or **6b** do not show strong absorption at long wavelengths (*Fig. 1*), since the two π-substituents cannot interact with each other *via* the central s-*trans*-buta-1,3-diene subunit of **6a** or **6b**.

Scheme 2



2.1.2. *With* t-*Bu or Me Groups at C(8)*. The electrophilic chlorination of heptalene **7** was performed as described for **4**. However, 1-(chloromethyl)heptalene-dicarboxylate **8** was formed in only 25% yield (*Scheme 3*), and it was impossible to separate **8** from non-reacted **7** (recovered in 35% yield) by column chromatography. The ^{1}H-NMR data of the mixture **7**/**8** showed an *AB* system at 4.25 and 3.95 ppm ($J_{AB} = 13.7$ Hz), which is characteristic for $ClCH_2$–C(1) of heptalene-4,5-dicarboxylates. So, it was easy to determine the amount of **7** and **8** from the mixture. Heating the mixture **7**/**8** with $P(OEt)_3$ at 130° for 4 h did not lead to the corresponding phosphonate. Therefore, we had to search for another way to introduce the second π-substituent at C(1). *Basu et al.* [5] (see also [6]) reported that the reaction of α,β-unsaturated esters with aldehydes in the presence of *t*-BuOK in *t*-BuOH lead to the formation of a second s-*trans*-conjugated C=C bond in γ-position. *Dehmlow* and *Shamount* [7] found that, in similar reactions,

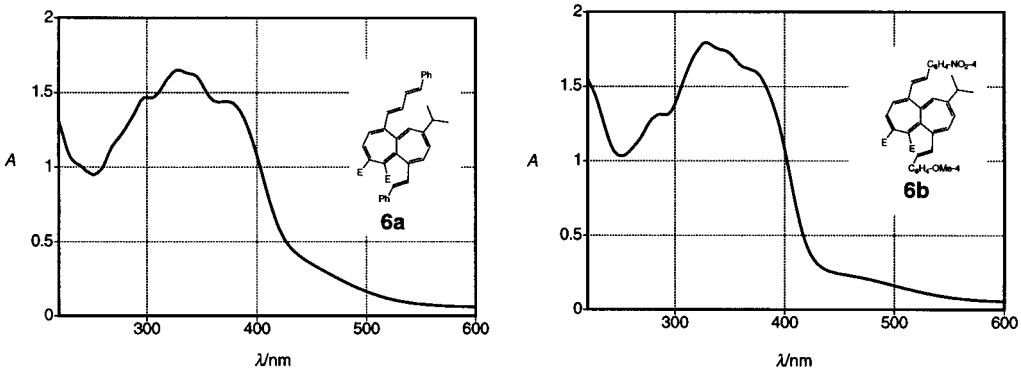
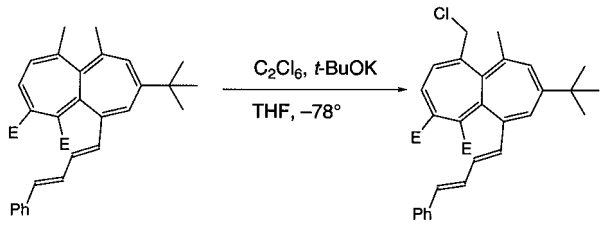


Fig. 1. *UV/VIS Spectra* (hexane) *of heptalene* **6a** *and* **6b**

Scheme 3



7 **8** (25%)[a])

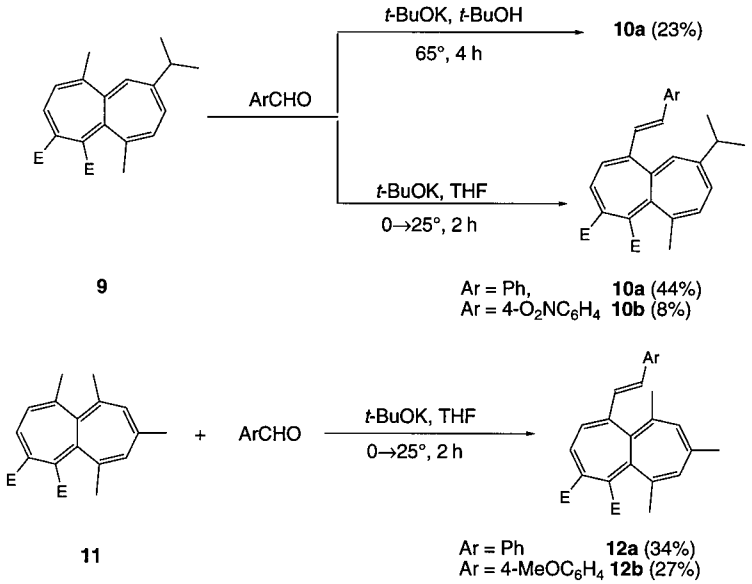
[a]) Starting heptalene **7** was still present in an amount of 35%.

K_2CO_3 can act as a base, when the reactions are performed in toluene in the presence of phase-transfer catalysts.

To examine whether these procedures are also applicable to 1-methylheptalene-4,5-dicarboxylates, we chose our standard heptalene **9** as model compound. Treatment of **9** with PhCHO in the presence of *t*-BuOK in *t*-BuOH at 65° for 4 h (*Scheme 4*) gave indeed the 1-styrylheptalene-dicarboxylate **10a** in 23% yield. Replacing *t*-BuOH with THF and lowering the temperature to $0 \rightarrow 25°$ augmented the yield of **10a** to 44%. On the other hand, under the same conditions, 4-nitrostyrylheptalene-dicarboxylate **10b** could be obtained in only 8% yield. The application of the same procedure to dimethyl 1,6,8,10-tetramethylheptalene-4,5-dicarboxylate (**11**) provided 1-styrylheptalene-dicarboxylate **12a** and its derivative **12b** in moderate yields. These results demonstrate that, in principle, a simple method is at our disposal for the introduction of styryl substituents at C(1) of 1-methylheptalene-4,5-dicarboxylates in just one step with similar yields as compared to our earlier, at minimum three-step, procedure [2].

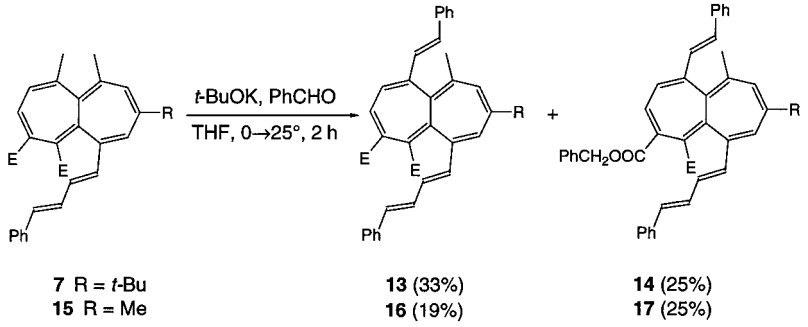
As expected, reaction of heptalene **7** with PhCHO and *t*-BuOK in THF afforded the 1,6-di-π-substituted heptalene **13** in 33% yield and, in addition, the transesterified heptalene-dicarboxylate **14** in 25% yield (*Scheme 5*). The formation of **14** is not surprising, since the *Cannizzaro* reaction of PhCHO takes place under basic condition to give $PhCH_2O^-$, which attacks MeOCO–C(4) of **13** to form the transesterification product **14**. The separation of **13** and **14** could easily be realized by column

Scheme 4



chromatography on silica gel, since **13** (R_f(hexane/Et_2O 1:1) 0.30) and **14** (R_f(hexane/Et_2O 1:1) 0.41) showed sufficiently different R_f in TLC. The ^{1}H-NMR spectrum ($CDCl_3$) of **13** resembled very much that of **14** with the difference that **14** exhibited PhCH_2OOC–C(4) as a *singlet* at 5.19 and the *singlet* of *Me*OCO–C(5) at 3.35 ppm, while **13** showed two *singlets* of *Me*OCO–C(4) and MeOCO–C(5) at 3.75 and 3.55 ppm. Under the same conditions, the reaction of the trimethylheptalene-dicarboxylate **15** with PhCHO led to the formation of the 1,6-di-π-substituted derivatives **16** (19%) and **17** (25%). As expected, there is nearly no difference in the UV/VIS spectra of **13**, **14, 16**, and **17** (*Fig. 2*). All four heptalenes exhibited Band I as a weak shoulder at *ca.* 420 nm, followed by the much more intense shoulder of Band II at *ca.* 350 nm, which is just recognizable at the long-wavelength flank of Band III. The latter one, appearing at 324 nm, represents the dominating absorption band in the spectrum. However, as it was already recognizable in the UV/VIS spectra of the i-Pr-

Scheme 5



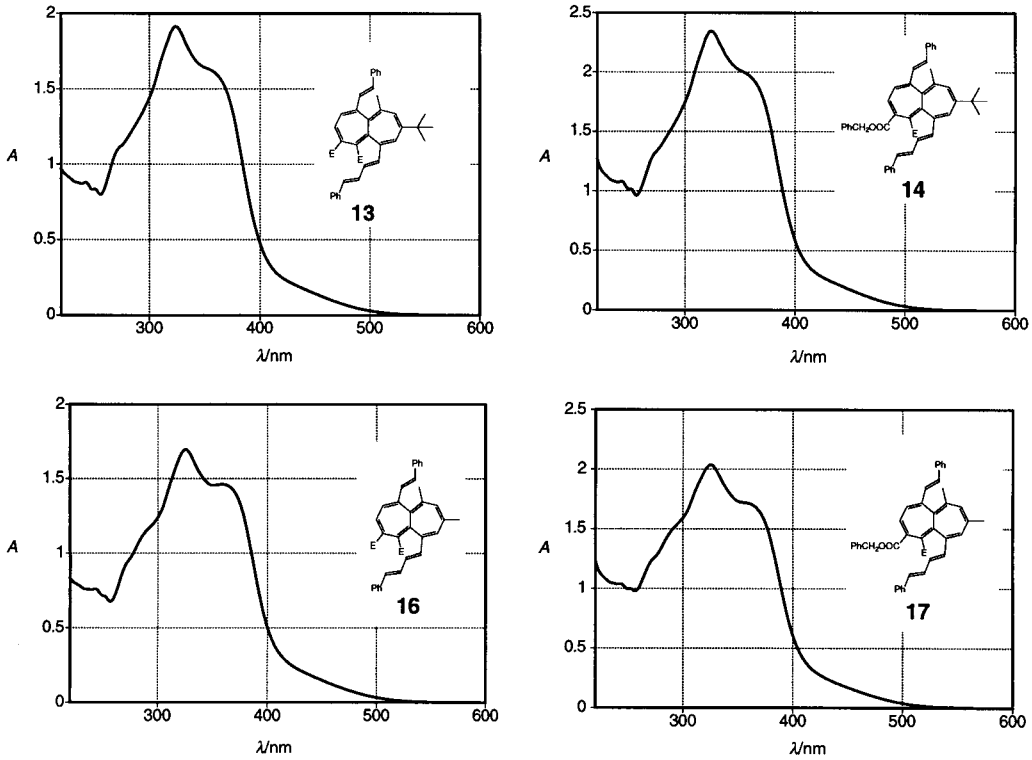


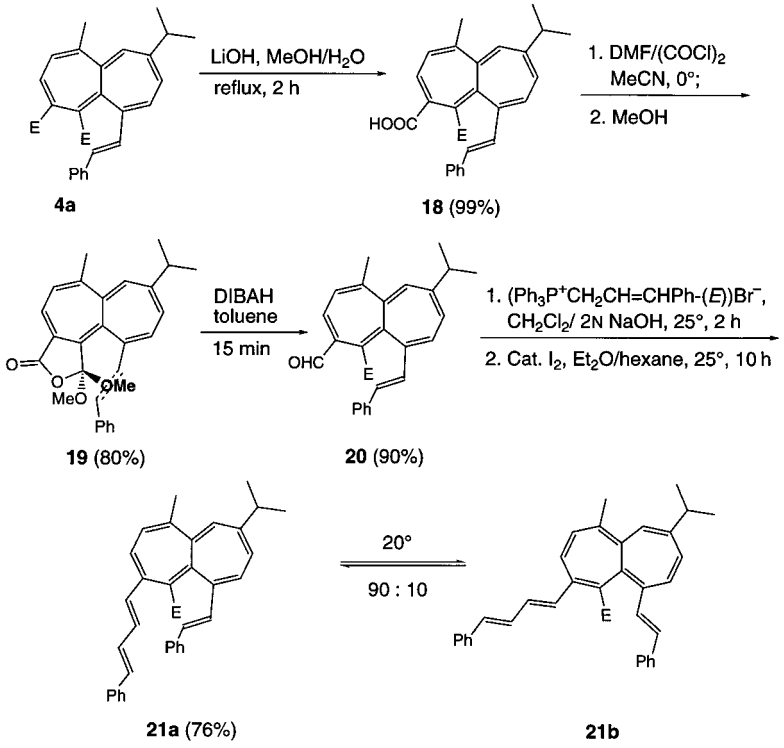
Fig. 2. *UV/VIS Spectra* (hexane) *of* **13, 14, 16,** *and* **17**

substituted heptalenes **6a** and **6b**, the intensity of Band II of **13**, **14**, **16**, and **17** is strongly enhanced as compared with corresponding heptalenes mono-π-substituted at C(1) or C(6) (*cf.* Fig. 8, b, as well as Fig. 10, c and e in [8]). Moreover, a comparison of the position of Band II of **6a** and **6b** with that of **13**, **14**, **16**, and **17** discloses a hypsochromic shift by *ca.* 25 nm for the latter four heptalenes with four substituents in the *peri*-positions. This general finding is in agreement with smaller torsion angles of **6a** and **6b**, which carry only three *peri*-substituents. Neither irradiation nor heating of **13**, **14**, **16**, or **17** led to the formation of the corresponding DBS isomers in detectable amounts (HPLC). This means that, at temperatures above 25°, the thermal equilibrium of all these 1,6-di-π-substituted heptalenes and their DBS isomers are to more than 99% on the side of the off-state, where the two π-substituents are not directly interacting with each other *via* the central s-*trans*-butadiene subunit of the heptalene core.

2.2. *4,6-Di-π-Substituted Heptalenes.* The transformation of the MeOCO group at C(4) of heptalene **4a** into an extented π-substituent was achieved according to established methods in our group. Selective saponification of MeOCO–C(4) of heptalene **4a** gave, in nearly quantitative yield, the mono-acid **18**, which was cyclized to pseudo-ester **19** under *Stadler* conditions. The controlled reduction of **19** with 1 equiv. of DIBAH in toluene at $-80°$ for 15 min gave the expected carbaldehyde **20**. The subsequent *Wittig* reaction of **20** in a two-phase system (CH_2Cl_2/2N NaOH) proceeded

smoothly and gave the 4,6-di-π-substituted heptalene **21a**, which is in thermal equilibrium with 10% of its DBS isomer **21b** at room temperature (*Scheme 6*). The torsion angle of the involved s-*trans*-butadiene subunit is *ca.* 118°, which should lead to a reduction of conjugation by *ca.* 60% [8]. Therefore, although the two π-substituents in **21b** are linked to each other through the s-*trans*-butadiene subunit of the heptalene core, the two π-substituents still interact more or less independently with the heptalene π-system. Indeed, the UV/VIS spectra of **21a** and **21b** resemble each other (*Fig. 3*). In other words, the thermal equilibrium of 4,6-di-π-substituted **21a**/**21b** is not very effective with respect to changes in the chromism.

Scheme 6



2.3. *6,9-Di-π-Substituted Heptalene.* Heptalenes such as **22** carry Me substituents always in allylic positions, so it should be possible to functionalize such groups. However, former attempts [2] to functionalize dimethyl 9-isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate, either by bromination with NBS or oxidation with SeO_2 in toluene, led to the formation of the desired products in only very poor yields. Therefore, we were not surprised when we found that heating of heptalene **22** with SeO_2 in toluene for 4 h led to only trace amounts of the carbaldehyde **23** ($< 5\%$), but $> 70\%$ of heptalene **22** could be recovered. The oxidation with SeO_2 worked much better in dioxane as solvent. Carbaldehyde **23** was obtained with good yield under this condition. The subsequent *Wittig* reaction in the two-phase system smoothly converted

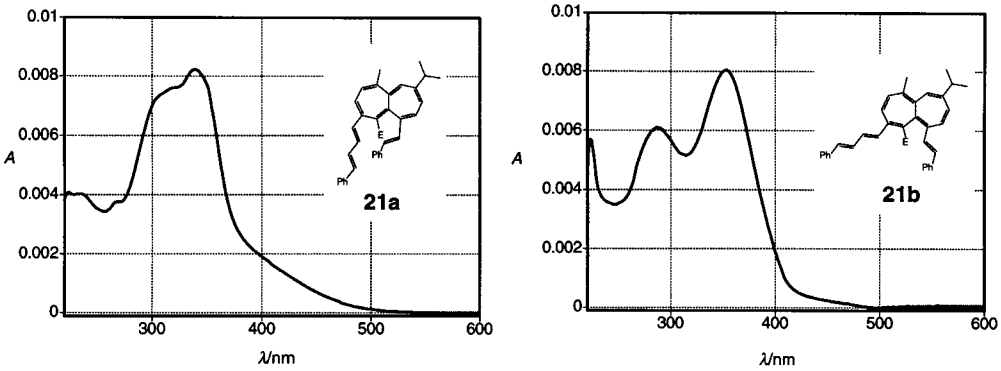
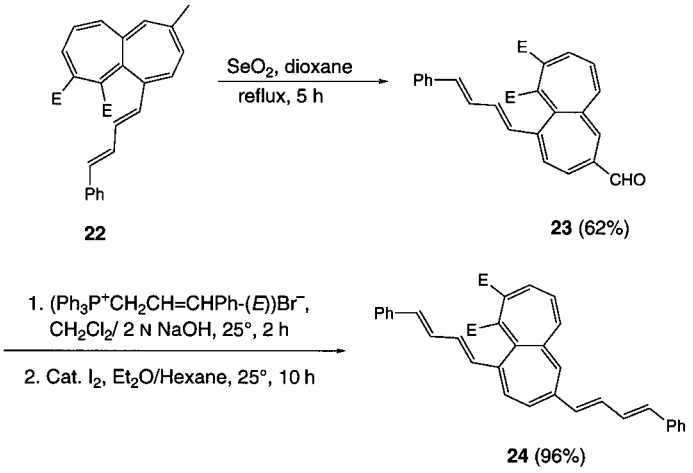


Fig. 3. *UV/VIS Spectra* (hexane/CH_2Cl_2) *of heptalenes* **21a** *and* **21b**

carbaldehyde **23** to 6,9-di-π-substituted heptalene-dicarboxylate **24** (*Scheme 7*). The ^{1}H-NMR spectrum of **23** displayed the signals of the side chain at C(6) as typical s-*trans*-buta-1,3-dienyl substituent with H–C(3′) at 6.82 ppm (*dd*, $J(3',4') = 15.5$, $J(2',3') = 10.7$) and H–C(2′) at 6.63 ppm (*dd*, $J(1',2') = 15.5$, $J(2',3') = 10.7$). Unfortunately, the signals of the butadienyl side chain at C(6) of di-π-substituted heptalene **24** were similar to that of heptalene **22**, *i.e.*, the signals of H–C(1′) and H–C(2′) were too close together at 6.48 ppm to clearly recognize the coupling constants. The conformations of the side chains of **24** were, therefore, confirmed by an X-ray crystal-structure analysis (*Fig. 4*), which revealed that both butadienyl groups were indeed s-*trans*-configured, and they were in s-*trans*-configurations with respect to the relevant C=C bonds of the heptalene core. There is a long-wavelength absorption in the UV/VIS spectra of **24**, but neither photochemical nor thermal treatment of **24** led to the formation of its DBS isomer. Moreover, there is an evident difference in the UV/VIS spectra of the on-state situation of **24** (*Fig. 5*) and that of methyl 1,4-bis[(1*E*,3*E*)-4-

Scheme 7



phenylbuta-1,3-dienyl]-9-isopropyl-6-methylheptalene-5-carboxylate (see Fig. 4 in [1]), which is comparable with **24**, but carries the MeOCO group at the same ring as the butadienyl moieties. The relative intensity of Band I in relation to the intensity of Band III is much larger in the latter heptalene as compared with **24**.

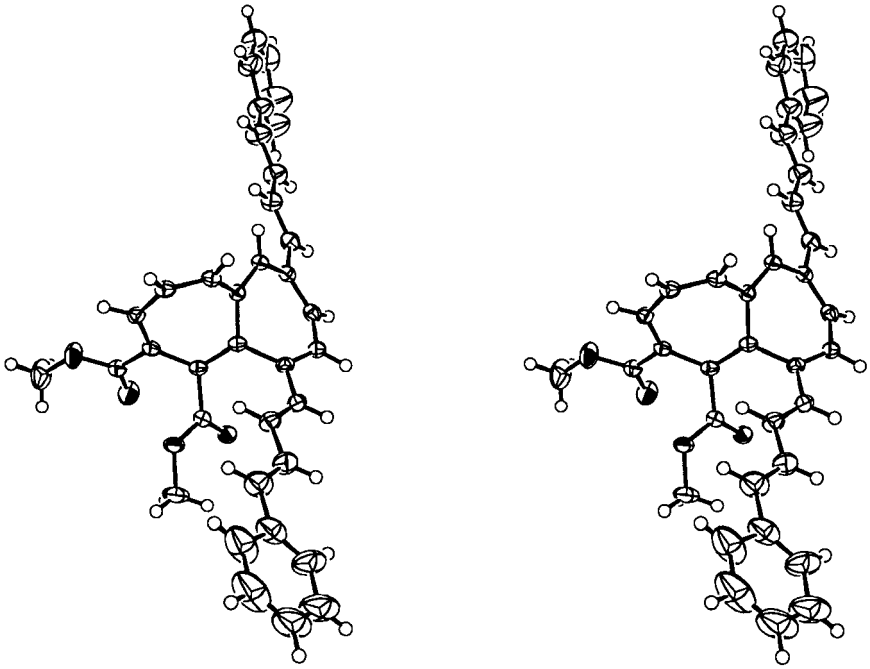


Fig. 4. *Stereoscopic view of the X-ray crystal structure of heptalene* **24**

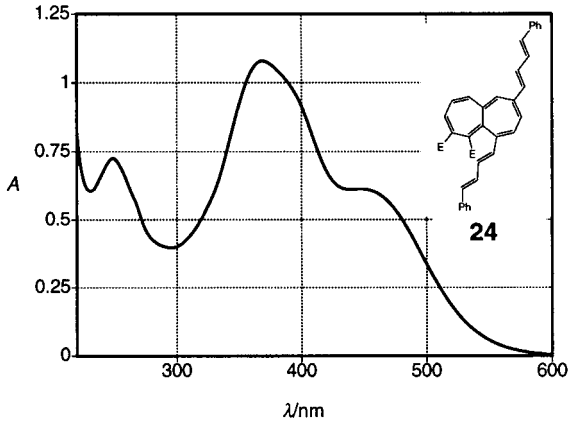


Fig. 5. *UV/VIS Spectra of heptalene* **24**

3. Concluding remarks. – Our results confirm that enhanced conjugation *via* s-cis-buta-1,3-diene subunits in the heptalene core is much more effective than that *via* corresponding s-*trans*-buta-1,3-diene subunits. The DBS processes, which turn on or off enhanced conjugation *via* the s-*cis*-buta-1,3-diene subunits of heptalenes, are accompanied by 'on- or off-switching' of observable properties, such as chemical shifts and coupling constants, or UV/VIS absorption bands. Thus, a further step has been achieved towards new systems for molecular switches or data storage systems.

We thank Dr. *A. Linden* for the X-ray crystal diffraction analyses, Prof. *M. Hesse* and his co-workers for mass spectra, our NMR department for NMR support and 2 D-NMR measurements, and our analytical laboratory for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [3]. Azulene **3a** and **3b** were available from [3]. Heptalenes **4a** and **4b** were synthesized according to [4]. And heptalenes **7**, **15**, and **22** were available from our previous work [9].

1. Syntheses of Heptalenes. – 1.1 *Dimethyl 1-(Chloromethyl)-9-isopropyl-6-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**5a**). At $-78°$, to the stirred soln. of heptalene **4a** (1.286 g, 3.0 mmol) and C_2Cl_6 (3.55 g, 15 mmol) in THF (30 ml) was added the soln. of *t*-BuOK (1.35 g, 12 mmol) in THF (15 ml) during 40 min. Stirring was continued at $-78°$ for 2 h before H_2O was added to quench the reaction. Extraction with Et_2O, followed by CC (silica gel; hexane/Et_2O 3 : 1), provided 1.26 g (90.7%) of **5a**. Yellow crystals. M.p. 116.4–116.9° (hexane). R_f (hexane/Et_2O 1 : 1): 0.33. UV/VIS (hexane): λ_{max} 350 (sh, 4.07), 306 (4.38), 257 (4.40); λ_{min} 279 (4.24), 226 (4.29). IR (KBr): 2959*m*, 1720*s*, 1434*m*, 1255*s*, 1229*m*, 1195*m*, 1162*w*, 1085*m*, 1051*m*, 964*w*, 751*m*, 694*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.64 (*d*, *J*(2,3) = 6.3, H–C(3)); 7.33 (*m*, 2 arom. H); 7.26 (*m*, 2 arom. H); 7.20 (*m*, 1 arom. H); 6.85 (*d*, *J* = 16.2, CH=C*H*–C(6)); 6.65 (*d*, *J*(2,3) = 6.3, H–C(2)); 6.55 (*d*, *J* = 16.2, C*H*=CH–C(6)); 6.47 (*d*, *J*(7,8) = 6.9, H–C(7)); 6.43 (*d*, *J*(7,8) = 6.9, H–C(8)); 6.02 (*s*, H–C(10)); 4.19, 4.12 (*AB*, J_{AB} = 13.2, CH_2Cl); 3.73, 3.49 (2*s*, *M*eOCO); 2.55 (*sept.*, *J* = 6.8, Me_2CH); 1.12, 1.09 (2*d*, *J* = 6.9, *Me*$_2$CH). EI-MS: 464/462 (6/18, $M^{+\bullet}$), 427 (18, $[M-Cl]^+$), 405/403 (8/24, $[M-MeOCO]^+$).

1.2. *Dimethyl 9-Isopropyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-6-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**6a**). Compound **5a** (325 mg, 0.7 mmol) and NaI (105 mg, 0.7 mmol) in $P(OEt)_3$ (8 ml) were heated at 130° for 2 h. After filtration, the excess $P(OEt)_3$ was removed under reduced pressure to leave an orange oil, which was then dissolved in THF (5 ml). To this soln. at $-78°$ was added 2N THF solution of $NaN(SiMe_3)_2$ (0.4 ml, 0.8 mmol), and, after 20 min, cinnamaldehyde (0.53 ml, 4.2 mmol) was added. The mixture was warmed within 4 h to 25°, and H_2O was added to quench the reaction. Extraction with Et_2O and normal workup resulted in a yellow residue, which was further purified by CC (silica gel; hexane/Et_2O 9:1) to give **6a** (190 mg, 50.1%). Orange crystals. M.p. 210.4–211.3° (Et_2O/hexane). R_f (hexane/Et_2O 1 : 1) 0.32. UV/VIS (hexane; see also *Fig. 1*): λ_{max} 420 (sh, 4.05), 380 (sh, 4.50), 328 (4.57), 299 (4.52); λ_{min} 303 (4.52), 251 (4.33). IR (KBr): 2957*w*, 1718*s*, 1596*w*, 1534*w*, 1508*w*, 1434*m*, 1260*s*, 1202*w*, 1086*w*, 1051*w*, 987*w*, 749*m*, 691*w*. ^{1}H-NMR (600 MHz, $CDCl_3$)[1]): 7.74 (*d*, *J*(2,3) = 6.8, H–C(3)); 7.52 (*m*, 4 arom. H); 7.26 (*m*, 4 arom. H); 7.17 (*m*, 2 arom. H); 6.87 (*d*, *J* = 16.0, CH=C*H*–C(6)); 6.77 (*dd*, *J*(3′,4′) = 15.5, *J*(2′,3′) = 10.7, H–C(3′)); 6.54 (*d*, *J*(1′,2′) = 15.0, H–C(1′)); 6.53 (*m*, H–C(7,8)); 6.53 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 6.50 (*d*, *J* = 16.0, C*H*=CH–C(6)); 6.47 (*d*, *J*(2,3) = 6.9, H–C(2)); 6.46 (*dd*, *J*(1′,2′) = 15.5, *J*(2′,3′) = 10.7, H–C(2′)); 5.98 (*s*, H–C(10)); 3.74, 3.50 (2*s*, MeOCO); 2.57 (*sept.*, *J* = 6.8, Me_2CH); 1.13, 1.11 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.58, 167.10 (2*s*, MeOCO); 150.09 (*s*); 142.91 (*s*); 139.74 (*d*); 137.92 (*s*); 137.12 (*s*); 136.84 (*s*); 135.52 (*d*); 133.57 (*d*); 132.98 (*d*); 131.75 (*s*); 130.61 (*s*); 130.06 (*d*); 128.56 (*d,* 4 arom. C); 128.38 (*d,* 2 arom. C); 128.32 (*d*); 128.19 (*d*); 127.97 (*d*); 127.91 (*d*); 127.34 (*d*); 127.24 (*s*); 126.54 (*s*); 126.44 (*d,* 4 arom. C); 125.77 (*d*); 52.08, 51.95 (2*q*, MeOCO); 35.85 (*d*, Me_2CH); 23.06, 22.20 (2*q*, *Me*$_2$CH). CI-MS: 544 (18), 543 (47, $[M+1]^+$), 511 (100, $[(M+1)-MeOH]^+$). Anal. cal. for $C_{37}H_{34}O_4$ (542.68): C 81.89, H 6.31; found: C 81.52, H 6.47.

1.3. *Dimethyl 1-(Chloromethyl)-9-isopropyl-6-[(*E*)-2-(4-methoxyphenyl)ethenyl]heptalene-4,5-dicarboxylate* (**5b**). The chlorination of **4b** (0.803 g, 1.75 mmol) with C_2Cl_6 (2.07 g, 8.75 mmol) in the presence of *t*-BuOK (0.786 g, 7.0 mmol) in THF was achieved as described for **4a** to give **5b** (776 mg, 90%). Yellow crystals. M.p.

[1]) The C-atoms of the butadienyl side chain are indicated with primed numbers.

147.7–148.9° (hexane). R_f (hexane/Et_2O 1:1): 0.33. UV/VIS (hexane): λ_{max} 318 (4.35), 256 (4.35); λ_{min} 284 (4.22), 231 (4.29). IR (KBr): 2958*w*, 1718*s*, 1606*w*, 1572*w*, 1511*m*, 1435*w*, 1254*s*, 1174*m*, 1088*w*, 1036*w*, 965*w*, 831*w*, 794*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.64 (*d*, *J*(2,3) = 6.2, H–C(3)); 7.28 (*d*-like, *J* = 8.8, 2 arom. H); 6.80 (*d*-like, *J* = 8.8, 2 arom. H); 6.73 (*d*, *J* = 16.1, CH=C*H*–C(6)); 6.65 (*d*, *J*(2,3) = 6.2, H–C(2)); 6.49 (*d*, *J* = 16.1, C*H*=CH–C(6)); 6.45 (*d*, *J*(7,8) = 6.8, H–C(7)); 6.38 (*d*, *J*(7,8) = 6.8, H–C(8)); 6.01 (*s*, H–C(10)); 4.20, 4.11 (*AB*, J_{AB} = 13.0, CH_2Cl); 3.79, 3.74 (2*s*, *Me*OCO); 3.49 (*s*, *Me*OC_6H_4); 2.54 (*sept.*, *J* = 6.9, Me_2CH); 1.12, 1.08 (2*d*, *J* = 6.9, *Me*$_2$CH). EI-MS: 494/492 (12/35, $M^{+\cdot}$), 457 (56, $[M-Cl]^+$), 435/433 (21/68, $[M-MeOCO]^+$).

1.4. *Dimethyl 9-Isopropyl-6-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-4,5-dicarboxylate* (**6b**). The transformation of **5b** (250 mg, 0.51 mmol) to **6b** (150 mg, 50%) was performed as described for **5a** in **6a** (see *1.2*). Deep orange crystals. M.p. 174.6–175.4° (Et_2O). R_f (hexane/Et_2O 1:1) 0.14. UV/VIS (hexane, see also *Fig. 1*): λ_{max} 442 (sh, 3.74), 380 (4.54), 328 (4.59), 287 (4.45); λ_{min} 291 (4.45), 251 (4.35). IR (KBr): 2956*w*, 1718*s*, 1654*w*, 1592*m*, 1510*s*, 1436*w*, 1342*s*, 1254*s*, 1174*w*, 1087*w*, 1036*w*, 967*w*, 854*w*, 832*w*, 749*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.10 (*d*-like, 2 arom. H); 7.76 (*d*, *J*(2,3) = 6.6, H–C(3)); 7.45 (*d*-like, 2 arom. H); 7.23 (*d*-like, 2 arom. H); 7.10 (*d*, *J* = 15.8, CH=C*H*–C(1)); 6.76 (*d*-like, 2 arom. H); 6.75 (*d*, *J* = 16.0, CH=C*H*–C(6)); 6.65 (*d*, *J*(2,3) = 6.6, H–C(2)); 6.60 (*d*, *J* = 15.9, C*H*=CH–C(1)); 6.53 (*m*, H–C(7,8)); 6.45 (*d*, *J* = 16.1, C*H*=CH–C(6)); 5.98 (*s*, H–C(10)); 3.75 (*s*, 2 MeOCO); 3.51 (*s*, MeO); 2.57 (*sept.*, *J* = 6.8, Me_2CH); 1.12, 1.10 (2*d*, *J* = 6.8, *Me*$_2$CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.45, 166.91 (2*s*, MeOCO); 159.27 (*s*); 149.67 (*s*); 149.97 (*s*); 142.93 (*s*); 141.59 (*s*); 139.19 (*d*); 138.76 (*s*); 133.28 (*d*); 133.16 (*s*); 130.81 (*s*); 130.77 (*d*); 129.91 (*d*); 129.69 (*s*); 129.24 (*d*); 129.10 (*d*); 128.07 (*d*); 127.63 (*d*, 2 arom. C); 127.34 (*d*, 2 arom. C); 126.48 (*s*); 126.20 (*s*); 126.19 (*d*); 125.86 (*d*); 123.86 (*d*, 2 arom. C); 113.93 (*d*, 2 arom. C); 55.16 (*q*, MeO); 52.16, 52.01 (2*q*, MeO*C*O); 35.80 (*d*, Me_2CH); 23.05, 22.22 (2*q*, *Me*$_2$CH). CI-MS: 593 (37), 592 (100, $[M+1]^+$), 560 (52, $[M-MeOH]^+$), 532 (43). Anal. calc. for $C_{36}H_{33}NO_7$ (591.67): C 73.08, H 5.62, N 2.37; found: C 72.72, H 5.40, N 2.32.

1.5. *1-[(*E*)-2-Phenylethenyl]heptalene-4,5-dicarboxylates from the Corresponding 1-Methylheptalenes. General Procedure.* At 0°, to the stirred soln. of the 1-methylheptalene-4,5-dicarboxylate (0.20 mmol) and ArCHO (0.26 mmol) in THF (2.7 ml) was added 1M THF soln. of *t*-BuOK (0.26 ml, 0.26 mmol) dropwise. The mixture was then left at 25°, and stirring was continued for 90 min. The reaction was quenched by addition of an aq. soln. of NH_4Cl, and the mixture was then extracted with Et_2O. The residue of Et_2O extracts was chromatographed (silica gel; hexane/Et_2O/CH_2Cl_2 80:5:15), followed by recrystallization from CH_2Cl_2/hexane, to yield pure 1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylates.

1.5.1. *Dimethyl 9-Isopropyl-6-methyl-1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**10a**) [4]. Heptalene **9** (68.1 mg, 0.2 mmol) and PhCHO provided **10a** (38 mg, 44%). Yellow crystals. M.p. 148.2–150.0°.

1.5.2. *Dimethyl 9-Isopropyl-6-methyl-1-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-4,5-dicarboxylate* (**10b**). Heptalene **9** (68.1 mg, 0.2 mmol) and 4-nitrobenzaldehyde provided **10b** (8 mg, 8.4%). Yellow crystals. M.p. 213.4–214.8° (CH_2Cl_2/hexane). R_f(hexane/Et_2O 1:1) 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.16 (*d*, *J* = 8.8, 2 arom. H); 7.65 (*d*, *J*(2,3) = 6.5, H–C(3)); 7.49 (*d*, *J* = 8.8, 2 arom. H); 7.10 (*d*, *J* = 15.8, C*H*=C*H*–C(1)); 6.57 (*d*, *J* = 15.8, C*H*=CH–C(1)); 6.54 (*d*, *J*(2,3) = 6.5, H–C(2)); 6.40 (*d*, *J*(7,8) = 6.6, H–C(7)); 6.32 (*d*, *J*(7,8) = 6.6, H–C(8)); 5.89 (*s*, H–C(10)); 3.74, 3.72 (*s*, 2 MeOCO); 2.53 (*sept.*, *J* = 6.8, Me_2CH); 1.09, 1.07 (2*d*, *J* = 6.8, *Me*$_2$CH). EI-MS: 474 (28), 473 (100, $M^{+\cdot}$), 426 (15), 414 (26), 398 (42), 331 (62).

1.5.3. *Dimethyl 6,8,10-Trimethyl-1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**12a**) [4]. Heptalene **11** (163 mg, 0.5 mmol) and PhCHO provided **12a** (70 mg, 34%). Yellow crystals. M.p. 191–192.2° ([4]: 192.5–193.0°).

1.5.4. *Dimethyl 1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6,8,10-trimethylheptalene-4,5-dicarboxylate* (**12b**) [4]. Heptalene **11** (163 mg, 0.5 mmol) and 4-methoxybenzaldehyde provided **12b** (60 mg, 27%) as yellow crystals. M.p. 176–176.7° ([4]: 174.0–175.0°).

1.5.5. *Dimethyl 8-(*tert*-Butyl)-10-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**13**) *and 4-Benzyl 5-Methyl 8-(*tert*-Butyl)-10-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**14**). Heptalene **7** (36.2 mg, 0.075 mmol) and PhCHO afforded **13** (14 mg, 33%) and **14** (12 mg, 25%).

Data of **13**: yellow crystals. M.p. 118.2–119.0° (hexane). R_f(hexane/Et_2O 1:1) 0.30. UV/VIS (hexane; see also *Fig. 2*): λ_{max} 420 (sh, 3.80), 350 (sh, 4.60), 324 (4.65); λ_{min} 256 (4.27). IR (KBr): 3024*w*, 2950*w*, 1719*s*, 1538*w*, 1435*m*, 1391*w*, 1260*s*, 1216*w*, 1194*w*, 1087*w*, 1053*w*, 987*w*, 774*w*, 751*m*, 691*m*. ^{1}H-NMR (300 MHz, $CDCl_3$)[1]): 7.76 (*d*, *J*(2,3) = 6.5, H–C(3)); 7.36–7.10 (*m*, 10 arom. H); 6.92 (*d*, *J* = 15.8, CH=C*H*–C(1)); 6.69 (*dd*, *J*(2′,3′) = 10.5, *J*(3′,4′) = 15.5, H–C(3′)); 6.64 (*d*, *J*(2,3) = 6.2, H–C(2)); 6.56 (*s*, H–C(7)); 6.42 (*d*, *J*(3′,4′) = 15.3, H–C(4′)); 6.39 (*d*, *J*(1′,2′) = 15.5, H–C(1′)); 6.35 (*d*, *J* = 16.0, C*H*=CH–C(1)); 6.32 (*s*, H–C(9)); 6.19 (*dd*, *J*(2′,3′) = 10.5, *J*(1′,2′) = 15.2, H–C(2′)); 3.75, 3.55 (2*s*, 2 MeOCO)); 1.68 (*s*, Me–C(10)); 1.28 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.65, 167.24 (*s*, 2 MeO*C*O); 153.04 (*s*); 141.94 (*s*); 139.70 (*s*); 138.78 (*d*); 137.27

(*s*); 136.77 (*s*); 134.06 (*s*); 133.03 (*d*); 132.97 (*d*); 132.79 (*s*); 131.51 (*d*); 131.35 (*s*); 129.83 (*d*); 129.26 (*d*); 128.84 (*d*); 128.48 (*d*, 2 arom. C); 128.44 (*d*, 2 arom. C); 128.12 (*d*); 127.95 (*d*); 127.30 (*d*); 127.11 (*d*); 126.92 (*d*, 2 arom. C); 126.71 (*d*); 126.16 (*d*, 2 arom. C); 125.61 (*s*); 123.75 (*s*); 52.04, 51.75 (*q*, 2 *Me*OCO); 36.55 (*s*, Me_3C); 30.30 (*q*, Me_3C); 19.22 (*q*, Me–C(10)). CI-MS: 588 (21, $[M+NH_4]^+$), 572 (20), 571 (50, $[M+1]^+$), 540 (39), 539 (100).

Data of **14**: Yellow crystals. M.p. 120.3–121.2° (hexane). R_f(hexane/Et_2O 1:1) 0.41. UV/VIS (hexane; see also *Fig. 2*): λ_{max} 420 (sh, 3.75), 350 (sh, 4.60), 324 (4.67); λ_{min} 256 (4.28). IR (KBr): 3025*w*, 2962*w*, 1717*s*, 1538*w*, 1496*w*, 1448*w*, 1252*s*, 1172*w*, 1084*w*, 1051*w*, 986*w*, 773*w*, 750*m*, 692*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.79 (*d*, *J*(2,3) = 6.5, H–C(3)); 7.40–7.10 (*m*, 15 arom. H); 6.91 (*d*, *J* = 15.8, CH=C*H*–C(1)); 6.67 (*dd*, *J*(3′,4′) = 15.5, *J*(2′,3′) = 10.5, H–C(3′)); 6.63 (*d*, *J*(2,3) = 6.5, H–C(2)); 6.55 (*s*, H–C(7)); 6.40 (*d*, *J*(1′,2′) = 15.1, H–C(1′)); 6.39 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 6.38 (*d*, *J* = 15.8, C*H*=CH–C(1)); 6.31 (*s*, H–C(9)); 6.19 (*dd*, *J*(1′,2′) = 15.1, *J*(2′,3′) = 10.5, H–C(2′)); 5.19 (*s*, PhCH_2); 3.35 (*s*, *Me*OCO); 1.68 (*s*, Me–C(10)); 1.28 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 167.53, 166.53 (*s*, MeO*C*O and $PhCH_2OCO$); 153.01 (*s*); 142.18 (*s*); 140.19 (*s*); 138.93 (*d*); 137.27 (*s*); 136.77 (*s*); 135.73 (*s*); 134.23 (*s*); 133.06 (*d*); 133.03 (*d*); 132.76 (*s*); 131.46 (*s*); 131.41 (*d*); 129.84 (*d*); 129.09 (*d*); 128.82 (*d*); 128.48 (*d*, 2 arom. C); 128.44 (*d*, 2 arom. C); 128.31 (*d*, 2 arom. C); 128.13 (*d*); 128.01 (*d*, 2 arom. C); 127.99 (*d*); 127.92 (*d*); 127.29 (*d*); 127.11 (*d*); 126.93 (*d*, 2 arom. C); 126.72 (*d*); 126.16 (*d*); 125.50 (*s*); 124.06 (*s*); 66.68 (*t*, Ph*C*H_2); 51.56 (*q*, *Me*OCO); 36.56 (*s*, Me_3C); 30.29 (*q*, Me_3C); 19.21 (*q*, Me–C(10)). CI-MS: 664 (28, $[M+NH_4]^+$), 648 (37), 647 (83, $[M+1]^+$), 646 (9, $M^{+\cdot}$), 616 (46), 615 (100).

1.5.6. *Dimethyl 8,10-Dimethyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**16**) *and 4-Benzyl 5-Methyl 8,10-Dimethyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-1-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* (**17**). Heptalene **15** (35 mg, 0.08 mmol) and PhCHO afforded **16** (8 mg, 19%) and **17** (12 mg, 25%).

Data of **16**: Yellow crystals. M.p. 117.2–118.0° (CH_2Cl_2/hexane). R_f(hexane/Et_2O 1:1) 0.31. UV/VIS (hexane; see also *Fig. 2*): λ_{max} 420 (sh, 3.60), 358 (4.55), 325 (4.61); λ_{min} 351 (4.55), 257 (4.22). IR (KBr): 3022*w*, 2974*w*, 1717*s*, 1538*w*, 1496*w*, 1435*m*, 1259*s*, 1214*w*, 1194*m*, 1162*w*, 1088*m*, 1053*w*, 986*w*, 964*m*, 775*w*, 751*m*, 691*m*. ^{1}H-NMR (600 MHz, $CDCl_3$)[1]): 7.79 (*d*, *J*(2,3) = 6.5, H–C(3)); 7.34 (*m*, 2 arom. H); 7.29 (*m*, 2 arom. H); 7.26 (*m*, 2 arom. H); 7.25 (*m*, 2 arom. H); 7.20 (*m*, 1 arom. H); 7.16 (*m*, 1 arom. H); 6.93 (*d*, *J* = 15.8, CH=C*H*–C(1)); 6.70 (*dd*, *J*(3′,4′) = 15.3, *J*(2′,3′) = 10.6, H–C(3′)); 6.67 (*d*, *J*(2,3) = 6.5, H–C(2)); 6.42 (*d*, *J*(3′,4′) = 15.2, H–C(4′)); 6.39 (*d*, *J*(1′,2′) = 15.2, H–C(1′)); 6.36 (*d*, *J* = 15.8, C*H*=CH–C(1)); 6.32 (*s*, H–C(7)); 6.28 (*s*, H–C(9)); 6.25 (*dd*, *J*(1′,2′) = 15.2, *J*(2′,3′) = 10.5, H–C(2′)); 3.76, 3.57 (*s*, 2 MeOCO); 2.18 (*s*, Me–C(8)); 1.67 (*s*, Me–C(10)). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.90, 167.70 (*s*, 2 MeO*C*O); 142.54 (*s*); 140.03 (*s*); 140.02 (*s*); 139.54 (*d*, C(3)); 137.47 (*s*); 136.99 (*s*); 133.63 (*d*, C(4′)); 133.40 (*s*); 133.14 (*d*, *C*H=CH–C(1)); 132.95 (*s*); 132.09 (*d*, C(9)); 131.98 (*d*, C(7)); 131.78 (*d*, C(1′)); 131.64 (*s*); 130.52 (*d*, C(2′)); 129.06 (*d*, C(3′)); 128.79 (*d*, 2 atom. C); 128.77 (*d*, 2 aom. C); 128.60 (*d*, C(2)); 128.46 (*d*, 1 atom. C); 127.70 (*d*, 1 arom. C); 127.33 (*d*, CH=*C*H–C(1)); 127.23 (*d*, 2 arom. C); 126.50 (*d*, 2 arom. C); 126.14 (*s*); 121.95 (*s*); 52.42, 52.12 (*q*, 2 *Me*OCO); 25.55 (*q*, Me–C(8)); 19.29 (*q*, Me–C(10)). CI-MS: 547 (12), 546 (33, $[M+NH_4]^+$), 530 (16), 529 (46, $[M+1]^+$), 498 (35), 497 (100).

Data of **17**: Yellow crystals. M.p. 107–108°. R_f(hexane/Et_2O 1:1) 0.44. UV/VIS (hexane, see also *Fig. 2*): λ_{max} 420 (sh, 3.62), 358 (4.54), 325 (4.62); λ_{min} 256 (4.31). IR (KBr): 3024*w*, 2946*w*, 1715*s*, 1654*w*, 1538*w*, 1497*w*, 1448*w*, 1435*w*, 1398*w*, 1246*s*, 1213*m*, 1192*m*, 1162*m*, 1077*m*, 1051*w*, 1028*w*, 986*m*, 964*w*, 773*w*, 751*m*, 692*m*. ^{1}H-NMR (600 MHz, $CDCl_3$)[1]): 7.84 (*d*, *J*(2,3) = 6.5, H–C(3)); 7.42–7.16 (*m*, 15 arom. H); 6.94 (*d*, *J* = 15.8, CH=C*H*–C(1)); 6.70 (*dd*, *J*(3′,4′) = 15.3, *J*(2′,3′) = 10.5, H–C(3′)); 6.67 (*d*, *J*(2,3) = 6.5, H–C(2)); 6.42 (*d*, *J*(3′,4′) = 15.2, H–C(4′)); 6.40 (*d*, *J*(1′,2′) = 15.2, H–C(1′)); 6.37 (*d*, *J* = 15.8, C*H*=CH–C(1)); 6.33 (*s*, H–C(7)); 6.30 (*s*, H–C(9)); 6.25 (*dd*, *J*(1′,2′) = 15.2, *J*(2′,3′) = 10.5, H–C(2′)); 5.31, 5.15 (*AB*, J_{AB} = 12.4, PhCH_2); 3.37 (*s*, MeOCO–C(5)); 2.20 (*s*, Me–C(8)); 1.69 (*s*, Me–C(10)). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.75, 166.84 (*s*, MeO*C*O & $PhCH_2OCO$); 142.66 (*s*); 140.00 (*s*); 140.01 (*s*); 139.72 (*d*, C(3)); 137.47 (*s*); 136.99 (*s*); 136.07 (*s*); 133.58 (*d*, C(4′)); 133.38 (*s*); 133.16 (*d*, *C*H=CH–C(1)); 132.97 (*s*); 132.10 (*d*, C(9)); 131.97 (*d*, C(7)); 131.76 (*d*, C(1′)); 131.63 (*s*); 130.50 (*d*, C(2′)); 129.06 (*d*, C(3′)); 128.80 (*d*, 2 arom. C); 128.78 (*d*, 2 arom. C); 128.75 (*d*, 2 arom. C); 128.60 (*d*, 2 arom. C); 128.58 (*d*, C(2)); 128.46 (*d*, 1 arom. C); 128.43 (*d*, 1 arom. C); 127.67 (*d*, 1 arom. C); 127.34 (*d*, CH=*C*H–C(1)); 127.23 (*d*, 2 arom. C); 126.48 (*d*, 2 arom. C); 126.21 (*s*); 122.01 (*s*); 67.11 (*t*, Ph*C*H_2); 51.99 (*q*, *Me*OCO); 25.52 (*q*, Me–C(8)); 19.31 (*q*, Me–C(10)). CI-MS: 622 (28, $[M+NH_4]^+$), 606 (40), 605 (100, $[M+1]^+$), 604 (25, $M^{+\cdot}$), 574 (42), 573 (98), 497 (37).

1.6. *9-Isopropyl-5-(methoxycarbonyl)-1-methyl-6-[(*E*)-2-phenylethenyl]heptalene-4-carboxylic Acid* (**18**). The heptalene **4a** (0.53 g, 1.24 mmol) and $LiOH \cdot H_2O$ (1.84 g) were refluxed for 2 h in a mixture of MeOH (75 ml) and H_2O (11 ml). After cooling, 20 ml of H_2O was added. Acidification with 2N aq. HCl, followed by addition of another 100 ml of H_2O, resulted in a yellow precipitate, which was isolated by filtration. Subsequent

recrystallization from CH_2Cl_2/Et_2O yielded **18** (0.50 g, 99%). Yellow crystals. M.p. 199.2–199.8° (Et_2O). UV/VIS (CH_2Cl_2/hexane): λ_{max} 410 (sh, 3.60), 350 (sh, 3.05), 306 (4.41), 260 (4.40); λ_{min} 279 (4.25). IR (KBr): 2960*m*, 1718*s*, 1686*s*, 1596*w*, 1569*w*, 1435*w*, 1286*m*, 1195*w*, 1165*w*, 1050*w*, 964*w*, 789*w*, 751*w*, 694*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.67 (*dd*, *J*(2,3) = 6.4, *J* = 0.9, H–C(3)); 7.34 (*m*, 2 arom. H); 7.27 (*m*, 2 arom. H); 7.20 (*m*, 1 arom. H); 6.86 (*d*, *J* = 16.1, CH=C*H*–C(6)); 6.56 (*d*, *J* = 16.1, C*H*=CH–C(6)); 6.43, 6.40 (*AB*, J_{AB} = 6.9, H–C(7), H–C(8)); 6.34 (*dd*, *J* = 1.4, *J*(2,3) = 6.4, H–C(2)); 5.94 (*s*, H–C(10)); 3.48 (*s*, MeOCO); 2.53 (*sept.*, *J* = 6.8, Me_2CH); 2.08 (*s*, Me–C(1)); 1.12, 1.09 (2*d*, *J* = 6.8, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 171.67 (*s*, COOH); 167.46 (*s*, MeO*C*O); 150.12 (*s*); 145.24 (*s*); 142.08 (*d*); 137.16 (*s*); 137.14 (*s*); 133.33 (*s*); 131.11 (*s*); 130.13 (*s*); 130.03 (*d*); 128.61 (*d*); 128.43 (*d*, 2 arom. C); 127.58 (*d*); 127.36 (*d*); 126.57 (*d*); 126.40 (*d*, 2 arom. C); 125.96 (*d*); 125.80 (*d*); 125.51 (*s*); 51.97 (*q*, *Me*OCO); 35.95 (*d*, Me_2CH); 25.91 (*q*, Me–C(1)); 22.91, 22.34 (2*q*, Me_2CH). EI-MS: 415 (26), 414 (89, $M^{+\bullet}$), 382 (29), 369 (86), 355 (100).

1.7. *8-Isopropyl-1,1-dimethoxy-6-methyl-11-[(*E*)-2-phenylethenyl]heptaleno[4,5-c]furan-3-one* (**19**). Treatment of **18** (250 mg, 0.60 mmol) in MeCN (2.7 ml) with the iminium salt from DMF (0.33 ml, 4.2 mmol) and $(COCl)_2$ (0.107 ml, 1.24 mmol) in MeCN (4 ml) was carried out as described in [10] [11] to yield **19** (206 mg, 80%). Deep orange crystals. M. p. 154.7–155.8° (hexane). R_f(hexane/Et_2O 1:1) 0.65. UV/VIS (hexane): λ_{max} 420 (sh, 3.60), 348 (4.19), 303 (4.38), 262 (4.44); λ_{min} 336 (4.18), 286 (4.33), 229 (4.31). IR (KBr): 2959*w*, 1772*s*, 1557*w*, 1287*m*, 1199*w*, 1162*w*, 1136*w*, 1061*w*, 962*w*, 919*m*, 809*w*, 779*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40 (*m*, 2 arom. H); 7.33 (*m*, 2 arom. H); 7.31 (*dd*, *J* = 0.7, *J*(4,5) = 6.6, H–C(4)); 7.23 (*m*, 1 arom. H); 6.95 (*d*, *J* = 16.0, CH=C*H*–C(11)); 6.74 (*d*, *J* = 16.0, C*H*=CH–C(11)); 6.55 (*d*, *J*(9,10) = 6.9, H–C(10)); 6.45 (*dd*, *J* = 1.4, *J*(4,5) = 6.6, H–C(5)); 6.33 (*d*, *J*(9,10) = 6.9, H–C(9)); 5.81 (*d*, *J* = 1.1, H–C(7)); 3.31, 3.19 (2*s*, MeO–C(1)); 2.50 (*sept.*, *J* = 6.8, Me_2CH); 2.19 (*dd*, *J* = 0.6, *J* = 1.4, Me–C(6)); 1.10, 1.07 (2*d*, *J* = 6.8, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.17 (*s*, C(3)); 151.67 (*s*); 139.94 (*s*); 137.39 (*s*); 136.03 (*s*); 134.03 (*d*); 132.21 (*s*); 130.39 (*d*); 130.04 (*d*); 129.50 (*s*); 129.34 (*s*); 129.25 (*s*); 128.45 (*d*, 2 arom. C); 127.99 (*d*); 127.81 (*d*); 127.39 (*d*); 126.98 (*d*); 126.45 (*d*, 2 arom. C); 124.73 (*d*); 119.03 (*s*, C(1)); 52.66, 50.50 (2*q*, MeO–C(1)); 36.34 (*d*, Me_2CH); 25.14 (*q*, *Me*–C(6)); 22.92, 22.59 (2*q*, Me_2CH). EI-MS: 429 (16), 428 (61, $M^{+\bullet}$), 369 (11), 121 (100). Anal. calc. for $C_{28}H_{28}O_4$ (428.53): C 78.48, H 6.59; found: C 78.60, H 6.57.

1.8. *Methyl 4-Formyl-9-isopropyl-1-methyl-6-[(*E*)-2-phenylethenyl]heptalene-5-carboxylate* (**20**). At −78°, to a stirred soln. of **19** (154 mg, 0.36 mmol) in toluene (13 ml) was added 1M DIBAH (0.36 ml, 0.36 mmol) in hexane. After 10 min, TLC indicated that all the starting material had been consumed. MeOH and H_2O were added subsequently to quench the reaction. Extraction, followed by CC (silica gel; hexane/Et_2O 3:1), yielded **19** (129 mg, 90%). Yellow crystals. M.p. 97.4–99.0° (hexane). ^{1}H-NMR (300 MHz, $CDCl_3$): 9.44 (*s*, CHO); 7.35 (*m*, 2 arom. H); 7.28 (*m*, 2 arom. H); 7.21 (*d*, *J*(2,3) = 6.1, H–C(3)); 7.19 (*m*, 1 arom. H); 6.85 (*d*, *J* = 16.1, CH=C*H*–C(6)); 6.58 (*d*, *J* = 16.1, C*H*=CH–C(6)); 6.45 (*dd*, *J* = 1.3, *J*(2,3) = 6.1, H–C(2)); 6.41 (*m*, H–C(7), H–C(8)); 5.94 (*s*, H–C(10)); 3.50 (*s*, MeOCO); 2.52 (*sept.*, *J* = 6.9, Me_2CH); 2.12 (*s*, Me–C(1)); 1.11, 1.07 (2*d*, *J* = 6.9, Me_2CH). EI-MS: 399 (27), 398 (100, $M^{+\bullet}$), 369 (28), 339 (67).

1.9. *Methyl 9-Isopropyl-1-methyl-4-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-6-[(*E*)-2-phenylethenyl]heptalene-5-carboxylate* (**21a**) and *Methyl 7-Isopropyl-5-methyl-2-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-10-[(*E*)-2-phenylethenyl]heptalene-1-carboxylate* (**21b**). The *Wittig* reaction of **20** (20 mg, 0.05 mmol) and (cinnamyl)(triphenyl)-phosphonium bromide (138 mg, 0.30 mmol) was carried out as described in [9] to give **21a**/**21b** (19 mg, 76%).

Data of **21a** (in thermal equilibrium in $CDCl_3$ at 25° with 10% of **21b**): yellow crystals. M.p. 157.0–158.3° (hexane). R_f (hexane/Et_2O 1:1) 0.75. UV/VIS (hexane/CH_2Cl_2; see also *Fig. 3*)[2]): λ_{max} 390, 340; λ_{min} 320. IR (KBr): 3024*w*, 2959*m*, 1714*s*, 1590*w*, 1494*w*, 1447*w*, 1432*w*, 1248*m*, 1216*m*, 1125*w*, 1053*w*, 989*m*, 748*m*, 691*m*. ^{1}H-NMR (600 MHz, $CDCl_3$, taken from the mixture with **21b**)[1]): 7.37 (*m*, 4 arom. H); 7.28 (*m*, 4 arom. H); 7.19 (*m*, 2 arom. H); 6.88 (*d*, *J* = 16.1, CH=C*H*–C(6)); 6.78 (*dd*, *J*(2′,3′) = 8.9, *J*(3′,4′) = 15.2, H–C(3′)); 6.62 (*d*, *J* = 16.1, C*H*=CH–C(6)); 6.55 (*d*, *J*(2,3) = 6.5, H–C(3)); 6.51 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 6.46 (*d*, *J*(7,8) = 6.8, H–C(8)); 6.43 (*d*, *J*(7,8) = 6.8, H–C(7)); 6.37 (*m*, H–C(1′), H–C(2′); 6.28 (*dd*, *J* = 1.3, *J*(2,3) = 6.5, H–C(2)); 5.94 (*s*, H–C(10)); 3.48 (*s*, MeOCO); 2.55 (*sept.*, *J* = 6.9, Me_2CH); 2.04 (*s*, Me–C(1)); 1.13, 1.10 (2*d*, *J* = 6.9, Me_2CH). CI-MS: 500 (37), 499 (100, $[M+1]^+$).

Data of **21b** (in thermal equilibrium in $CDCl_3$ at 25° with 90% of **21a**): UV/VIS (hexane/CH_2Cl_2; see also *Fig. 3*)[2]): λ_{max} 415, 360, 290; λ_{min} 315. ^{1}H-NMR (600 MHz, $CDCl_3$, taken from the mixture with **21a**)[1]): 7.64 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 7.43 (*m*, 4 arom. H); 7.32 (*m*, 4 arom. H); 7.23 (*m*, 2 arom. H); 7.02 (*dd*, *J*(2′,3′) = 10.7, *J*(1′,2′) = 15.5, H–C(2′)); 6.93 (*d*, *J* = 16.1, CH=C*H*–C(10)); 6.87 (*d*, *J*(3,4) = 11.9, H–C(4)); 6.79 (*dd*, *J*(2′,3′) = 10.7, J(3′,4′) = 15.5, H–C(3′)); 6.78 (*d*, *J*(8,9) = 10.9, H–C(9)); 6.72 (*d*, *J*(1′,2′) = 15.6, H–C(1′)); 6.59

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[2]) UV/VIS Spectra recorded during HPLC (*Waters*, model *911*) with the photodiode-array detector.

(*d*, *J* = 16.1, C*H*=CH–C(10)); 6.58 (*d*, *J*(3,4) = 11.9, H–C(3)); 6.54 (*d*, *J*(8,9) = 10.9, H–C(8)); 5.84 (*s*, H–C(6)); 3.58 (*s*, MeOCO); 2.61 (*sept.*, *J* = 6.9, Me_2CH); 1.84 (*s*, Me–C(5)); 1.10, 0.99 (2*d*, *J* = 6.9, Me_2CH).

1.10. *Dimethyl 9-Formyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylate* (**23**): The mixture of **22** (45 mg, 0.11 mmol) and SeO_2 (45 mg, 0.32 mmol) in dioxane (2,5 ml) was heated at 100° for 6 h. After filtration, dioxane was removed to leave a orange residue, which was then subjected to CC (silica gel; hexane/Et_2O 1:1) to give **23** (29 mg, 62%). Orange crystals. M.p. 209.0–210.3° (Et_2O). R_f(hexane/AcOEt 4:6) 0.59. UV/VIS (hexane): λ_{max} 440 (sh, 4.10), 368 (4.29), 330 (4.38), 284 (4.21), 244 (4.29); λ_{min} 353 (4.28), 293 (4.19), 267 (4.14), 230 (4.25). IR (KBr): 2950*w*, 1717*s*, 1684*s*, 1596*w*, 1558*w*, 1501*m*, 1436*w*, 1272*s*, 1164*m*, 1128*w*, 1054*w*, 1004*w*, 893*w*, 752*w*, 714*w*, 692*w*. ^{1}H-NMR (600 MHz, $CDCl_3$)[1]): 9.55 (*s*, CHO); 7.69 (*d*, *J*(2,3) = 6.4, H–C(3)); 7.39 (*m*, 2 arom. H); 7.32 (*m*, 2 arom. H); 7.25 (*m*, 1 arom. H); 7.24 (*d*, *J*(7,8) = 7.0, H–C(8)); 6.82 (*dd*, *J*(3′,4′) = 15.5, *J*(2′,3′) = 10.7, H–C(3′)); 6.67 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 6.63 (*dd*, *J*(1′,2′) = 15.3, *J*(2′,3′) = 10.4, H–C(2′)); 6.59 (*d*, *J*(7,8) = 7.0, H–C(7)); 6.55 (*dd*, *J*(1,2) = 10.3, *J*(2,3) = 6.4, H–C(2)); 6.54 (*d*, *J*(1′,2′) = 15.5, H–C(1′)); 6.30 (*s*, H–C(10)); 6.26 (*d*, *J*(1,2) = 10.2, H–C(1)); 3.74, 3.57 (2*s*, MeOCO). ^{13}C-NMR (150 MHz, $CDCl_3$)[3]): 192.70 (*d*, CHO); 167.22, 166.63 (2*s*, MeO*C*O); 144.82 (*d*, C(8)); 141.00 (*d*, C(3)); 139.47 (*s*); 137.60 (*s*); 136.94 (*s*); 136.71 (*s*); 136.51 (*d*, C(4′)); 134.87 (*d*, C(1)); 134.07 (*s*); 133.22 (*d*, C(2′)); 132.07 (*d*, C(1′)); 131.78 (*d*, C(2)); 131.37 (*s*); 128.71 (*d*, 2 arom. C); 128.27 (*d*, 1 arom. C); 128.05 (*d*, C(7)); 127.93 (*d*, C(3′)); 126.63 (*d*, 2 arom. C); 124.49 (*d*, C(10)); 52.40, 52.23 (2*q*, *Me*OCO). EI-MS: 427 (27), 426 (100, $M^{+\cdot}$), 394 (22, $[M-CO]^+$), 367 (35), 335 (64).

1.11. *Dimethyl 6,9-Bis[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]heptalene-4,5-dicarboxylate* (**24**). The *Wittig* reaction of **23** (27 mg, 0.053 mmol) with (cinnamyl)(triphenyl)phosphonium bromide (175 mg, 0.38 mmol) was carried out as described in [9] to yield **24** (32 mg, 96%). Orange crystals. M.p. 181.2–181.9° (hexane). R_f(hexane/Et_2O 1:1) 0.27. UV/VIS (hexane; see also *Fig. 4*): λ_{max} 450 (sh, 4.25), 368 (4.48), 249 (4.30); λ_{min} 296 (4.04). IR (KBr): 3024*w*, 2948*w*, 1735*s*, 1599*w*, 1492*w*, 1436*w*, 1272*s*, 1124*w*, 1052*w*, 981*m*, 884*w*, 776*w*, 749*m*, 692*w*. ^{1}H-NMR (600 MHz, $CDCl_3$)[4]): 7.69 (*d*, *J*(2,3) = 6.4, H–C(3)); 7.38 (*m*, 4 arom. H); 7.30 (*m*, 4 arom. H); 7.21 (*m*, 2 arom. H); 6.87 (*dd*, *J*(3″,4″) = 15.4, *J*(2″,3″) = 10.5, H–C(3″)); 6.81 (*dm*-like, *J*(3′,4′) = 15.5, H–C(3′)); 6.60 (*d*, *J*(3″,4″) = 15.5, H–C(4″)); 6.58 (*dd*, *J*(1″,2″) = 15.4, *J*(2″,3″) = 10.5, H–C(2″)); 6.57 (*d*, *J*(3′,4′) = 15.5, H–C(4′)); 6.53 (*dd*, *J*(1,2) = 10.2, *J*(2,3) = 6.3, H–C(2)); 6.52 (*d*, *J*(7,8) = 7.0, H–C(8)); 6.48 (*m*, H–C(1′,2′)); 6.43 (*d*, *J*(1″,2″) = 15.5, H–C(1″)); 6.42 (*d*, *J*(7,8) = 7.0, H–C(7)); 6.19 (*d*, *J*(1,2) = 10.2, H–C(1)); 6.08 (*s*, H–C(10)); 3.73, 3.56 (2*s*, MeOCO). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.50, 166.91 (2*s*, MeOCO); 140.64 (*s*); 140.48 (*d*, C(3)); 138.65 (*s*); 137.27 (*s*); 137.21 (*s*); 135.34 (*d*, C(1″)); 134.60 (*d*, C(1)); 134.27 (*s*); 133.91 (*d*, C(4′)); 133.23 (*d*, C(1′)); 133.17 (*d*, C(4″)); 132.55 (*s*); 131.15 (*d*, C(8)); 130.98 (*d*, C(2)); 130.37 (*s*); 130.22 (*d*, C(7)); 129.90 (*d*, C(2′)); 129.42 (*d*, C(2″)); 129.15 (*d*, C(3″)); 128.62 (*d*, C(3′)); 128.61 (*d*, 4 arom. C); 127.63 (*d*, 1 arom. C); 127.58 (*d*, 1 arom. C); 126.97 (*s*); 126.40 (*d*, C(10)); 126.36 (*d*, 2 arom. C); 126.34 (*d*, 2 arom. C); 52.30, 52.13 (2*q*, MeOCO). CI-MS: 544 (32, $[M+NH_4]^+$), 527 (100, $[M+1]^+$), 526 (8, $M^{+\cdot}$), 499 (23).

2. X-Ray Crystal-Structure Determination[5]) **of 24.** – The calculations for **24** were performed using the TEXSAN crystallographic software package. The data collection and refinement parameters are given in the *Table*. For other experimental detail, see [9].

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[3]) One quaternary-C signal was hidden under the other signals.

[4]) The C-atoms of the buta-1,3-dienyl side chain at C(6) are indicated with primed numbers, and those of the buta-1,3-dienyl moiety at C(9) with double-primed numbers.

[5]) Crystallographic data (excluding structure factors) for the structures of compounds **24** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-134038. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table. *Crystallographic Data of* **24**

	24
Crystallized from	CH_2Cl_2/Et_2O/hexane
Empirical formula	$C_{36}H_{30}O_4 \cdot 0.5\ CH_2Cl_2$
Formula weight [g mol^{-1}]	569.10
Crystal color, habit	Red, prism
Crystal dimensions [mm]	$0.25 \times 0.28 \times 0.48$
Temp. [K]	173(1)
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
Reflections for cell determination	25
2θ Range for cell determination [°]	33–38
Unit cell parameters a [Å]	11.656(2)
b [Å]	14.135(2)
c [Å]	9.762(2)
α [°]	102.73(1)
β [°]	99.51(1)
γ [°]	85.40(1)
V [Å^3]	1545.6(5)
D_x [g cm^{-3}]	1.223
$\mu(\mathrm{MoK}_\alpha)$ [mm^{-3}]	0.161
2θ (max) [°]	55
Total reflections measured	7434
Symmetry-independent reflections	7087
Reflections used [$I > 2\sigma(I)$]	4617
Parameters refined	398
Final R	0.0723
wR	0.0705
Goodness of fit	3.483
Secondary extinction coefficient	$1.04(8) \times 10^{-6}$
Final Δ_{max}/σ	0.0002
$\Delta\varrho$ (max; min) [e Å^{-3}]	0.56; −0.48
σ (d(C–C)) [Å]	0.004–0.01

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