Formation of 6,10-Diphenyl-Substituted Heptalene-4,5-dicarboxylates

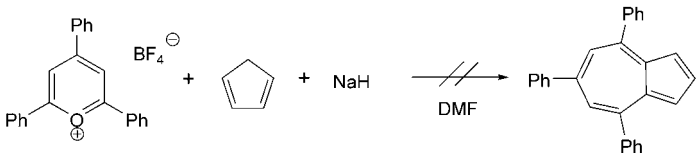
by **Xudong Jin**[1]), **Anthony Linden**, and **Hans-Jürgen Hansen***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
(phone: +41-1-635 42 30; fax: +41-1-635 68 12; e-mail: H.-J.H@access.unizh.ch)

It is shown that 4,8-diphenylazulene (**1**) can be easily prepared from azulene by two consecutive phenylation reactions with PhLi, followed by dehydrogenation with chloranil. Similarly, a Me group can subsequently be introduced with MeLi at C(6) of **1** (*Scheme 2*). This methylation led not only to the expected main product, azulene **2**, but also to small amounts of product **3**, the structure of which has been determined by X-ray crystal-structure analysis (*cf. Fig. 1*). As expected, the latter product reacts with chloranil at 40° in Et_2O to give **2** in quantitative yields. *Vilsmeier* formylation of **1** and **2** led to the formation of the corresponding azulene-1-carbaldehydes **4** and **5**. Reduction of **4** and **5** with $NaBH_4/BF_3 \cdot OEt_2$ in diglyme/Et_2O 1:1 and $BF_3 \cdot OEt_2$, gave the 1-methylazulenes **6** and **7**, respectively. In the same way was azulene **9** available from **6** *via Vilsmeier* formylation, followed by reduction of azulene-1-carbaldehyde **8** (*Scheme 3*). The thermal reactions of azulenes **1**, **6**, and **7** with excess dimethyl acetylenedicarboxylate (ADM) in MeCN at 100° during 72 h afforded the corresponding heptalene-4,5-dicarboxylates **11**, **12**, and **13**, respectively (*Scheme 4*). On the other hand, the highly substituted azulene **9** gave hardly any heptalene-4,5-dicarboxylate.

1. Introduction. – In the course of our investigations of the chemistry of highly substituted heptalene-4,5-dicarboxylates as precursors for new chiral ligand systems in homogeneous transition metal catalysis [1], we were interested in the synthesis of *peri*-phenylated azulenes as starting material for the formation of the corresponding heptalene-4,5-dicarboxylates. Unfortunately, the elegant synthesis of *Hafner* and *Kaiser* of 4,6,8-trimethylazulene [2] and other trisubstituted azulenes of this type (see, *e.g.*, [3]), cannot be applied to the synthesis of 4,6,8-triphenylazulene, starting with commercially available 2,4,6-triphenyl pyrylium tetrafluoroborate (*AVOCADO Research Chemicals Ltd.*) (*Scheme 1*). On the other hand, azulenes with substituents at 4-, 6-, and 8-position can be prepared according to *Hafner et al.* [4][5] by addition of R–Li reagents to azulenes. The thus formed dihydroazulenes can easily be dehydrogenated with chloranil (=2,3,5,6-tetrachlorobenzo-1,4-quinone) in EtOH or MeOH.

Scheme 1



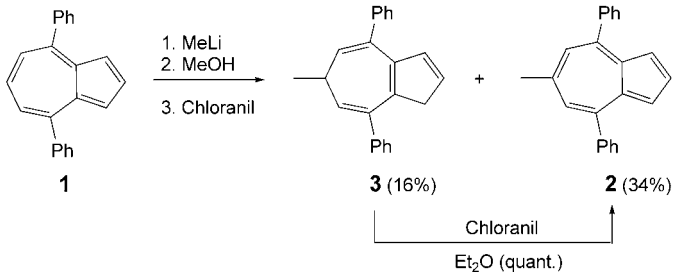
[1]) Part of the projected Ph.D. thesis of *X. J.*, University of Zurich, 2004. Present address: School of Chemical Science & Engineering, Liaoning University, 110036 P.R. China.

© 2005 Verlag Helvetica Chimica Acta AG, Zürich

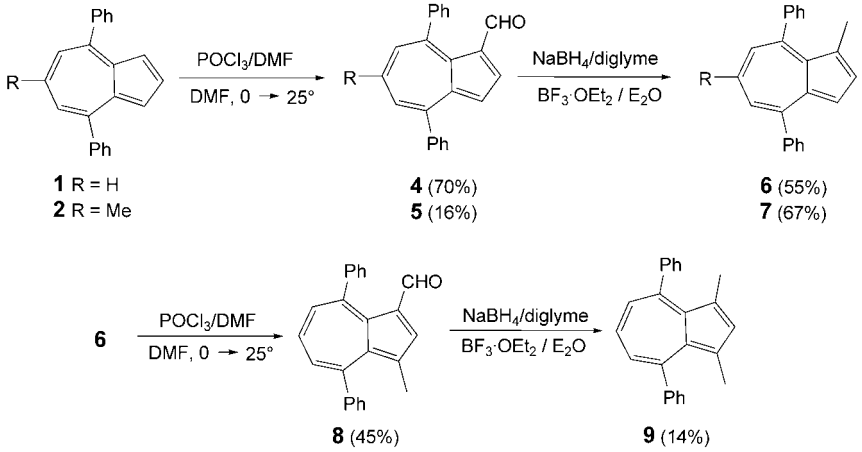
In this paper, we report the synthesis of 4,8-diphenylated azulenes with further Me substituents at C(1) and C(6) and their thermal reaction with dimethyl acetylenedicarboxylate (ADM), resulting in the formation of the corresponding heptalene-4,5-dicarboxylates.

2. Results and Discussion. – 2.1. *Chemistry.* We started with 4,8-diphenylazulene (**1**), which was obtained from azulene [6] by two consecutive phenylation reactions in an overall yield of 67% [4]. The introduction of a further Me substituent at C(6) was realized by treatment of **1** with MeLi, followed by dehydrogenation of the adduct with chloranil in MeOH [5]. Purification of the deep blue azulene **2** by chromatography on silica gel gave a second, orange-colored product, which turned out to be the corresponding dihydroazulene **3** (*Scheme 2*). The structure of **3** was evident from its ^{1}H- and ^{13}C-NMR spectrum (see *Exper. Part*)[2]). Since it could be crystallized from hexane/Et_2O, we also performed an X-ray crystal-structure analysis of **3** (*vide infra*).

Scheme 2



Scheme 3

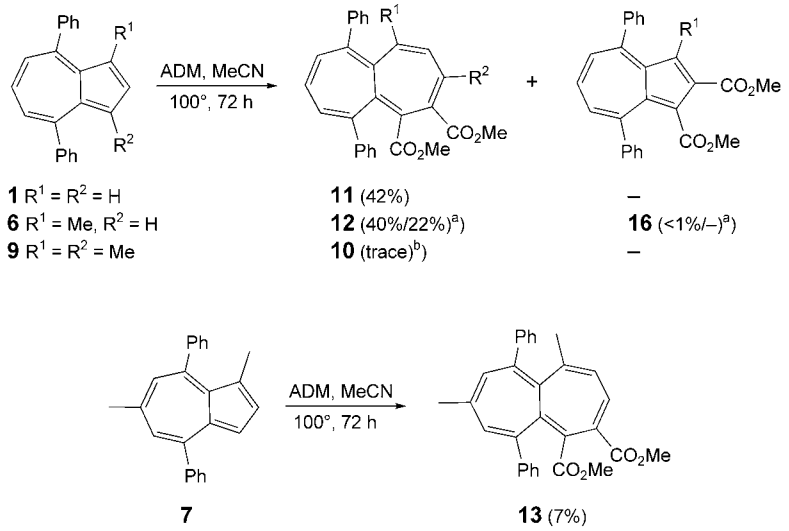


[2]) Moreover, compound **3** is energetically favored by 2.8 kcal · mol^{-1} (according to AM1 calculations) over its [1,5]-sigmatropic tautomer, the 2,6-dihydro compound, which represents the other possible product of protonation of the corresponding intermediary 6-hydro-6-methylazulenide.

The introduction of a further Me group at C(1) of **1** and **2** was performed by the established *Vilsmeier* borane reduction sequence (*Scheme 3*) [7], thus leading *via* the azulene-1-carbaldehydes **4** and **5** to the azulenes **6** and **7**, respectively. Azulene **6** was again subjected to the *Vilsmeier* borane reduction procedure to give aldehyde **8** and the further product 1,3-dimethylazulene **9** (see also *Scheme 3*).

The azulenes **1**, **6**, **7**, and **9** were heated with a twofold molar excess of ADM in MeCN in a closed *Schlenk* vessel under Ar at 100° (*Scheme 4*). Heptalenedicarboxylate formation was observed in all cases. However, azulene **9** gave only trace amounts of the expected heptalenedicarboxylate **10**, which could be identified, solely on the TLC plate by its correlated R_f value and its color. In the other three cases, the heptalene-4,5-dicarboxylates **11**, **12**, and **13**, respectively, were successfully isolated and spectroscopically characterized. Moreover, the heptalene-4,5-dicarboxylates **11** and **12** crystallized well and were subjected to an X-ray crystal-structure analysis (*vide infra*).

Scheme 4



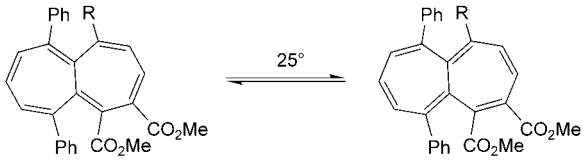
a) Second value corresponds to DMF, 170°, 48 h. b) Not enough to be isolated, but recognizable in TLC by its typical R_f value and the pale-yellow color of the spot.

The ^{1}H-NMR analysis of heated probes of the heptalenedicarboxylats **11** and **12** showed that the equilibrium mixtures at room temperature consisted mainly of **11** and **12**, respectively. Their DBS isomers **11′** and **12′** were present to an extent of 7–8%, in the case of **11**, and to <1% in the case of **12** (*Scheme 5*). Therefore, the irradiation experiments of **12** in toluene were conducted with a fluorescence lamp (λ_{max} (emiss.) 366 and 433 nm)[3]) at room temperature, but failed completely. The formation of **12′** was not observed.

---

[3]) Both heptalene-dicarboxylats **11** and **12**, show shoulders in hexane in the long-wavelength region of 385–400 nm (see *Exper. Part*).

Scheme 5



11 R = H (92 – 93%)[a]) **11'** (7 – 8%)[a])
12 R = Me (<99)[b]) **12'** (< 1%)

[a]) 93 : 7% in $CDCl_3$ and 92 : 8% in C_6D_6. [b]) In (D_6)acetone.

2.2. *X-Ray Analysis.* The X-ray crystal structure of the dihydroazulene **3** is shown in *Fig. 1*. The analysis of the structure of **3** showed a disordered molecule, that results from the superposition of mirror images of the molecule on the same crystallographic site. The disorder manifests itself only in the alternation of the double-bound position within the five-membered ring and, thus of the H-atoms associated with this ring. As a result, only averaged bond lengths of the C(1)–C(2)=C(3) part could be determined (for details, see *Exper. Part*). Nevertheless, the seven-membered ring of **3** shows a clear boat conformation, in which Me–C(6) has an equatorial orientation. That the same conformation of the seven-membered ring is present in solution at room temperature is indicatated by $^3J(H–C(5),H–C(6)) \approx {}^3J(H–C(6),H–C(7)) = 5.7$ Hz, typical for corresponding H,H torsion angles in the range of 120° (X-ray: ±132°). Moreover, the AM1-calculated H,H torsion angles at the five-membered ring amount to almost 60° (H_a–C(1)–C(2)–H and H_b–C(1)–C(2)–H) in agreement with a nearly perfect planar five-membered ring. Indeed, the ^{1}H-NMR data are also in agreement with a planar five-membered ring, since no visible coupling can be observed between the methylene group, which appears as a clear *AB* system with $^2J(AB) = 14.4$ Hz in the expected range of 3.2–3.6 ppm, and H–C(2) and H–C(3). The slightly broadened

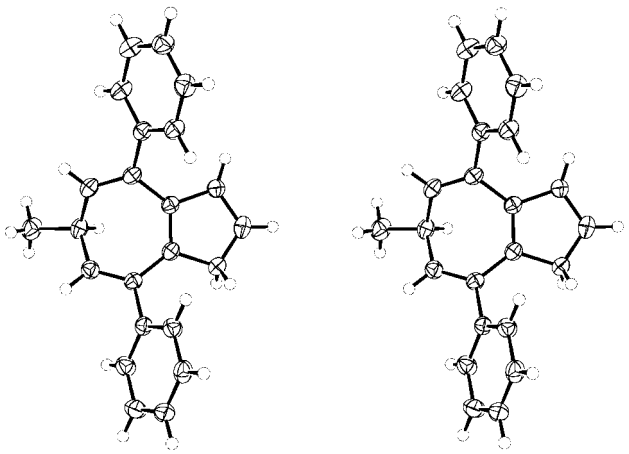


Fig. 1. *Stereoscopic view of the X-ray crystal structure of 1,6-dihydro-6-methyl-4,8-diphenylazulene* (**3**)

doublet for H–C(2) and H–C(3) with ^3J(H–C(2), H–C(3)) = 5.4 Hz indicates very small values for the vicinal and allylic coupling, respectively, with CH_2(1).

The asymmetric unit of **11** contains two symmetry-independent molecules. The molecules differ primarily in the relative orientation of the MeOCO substituent at C(4) with respect to the C(3)=C(4) bond. In one molecule, the C=O group of MeOCO–C(4) occupies more or less a s-*trans*-conformation (see *Fig. 2* and *Table 1*),

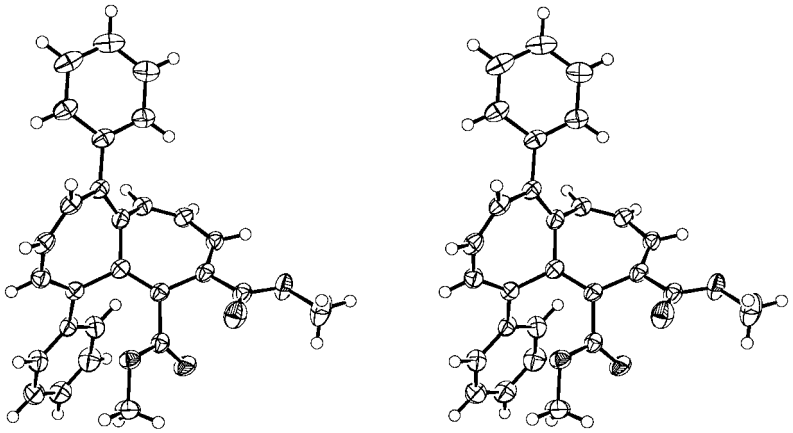
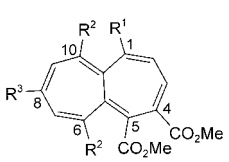
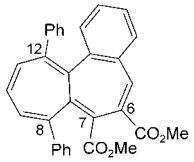


Fig. 2. *Stereoscopic view of the X-ray crystal structure of dimethyl 6,10-diphenylheptalene-4,5-dicarboxylate* (**11**; the s-*trans* conformation of MeOOC–C(4) in the (*P*) configuration of the heptalene skeleton is shown)

Table 1. *Characteristic Torsion Angles of X-Ray Crystal Structure Analyses of Heptalenedicarboxylates*



11, **12**, **14**



15

Compound	R in Heptalenedicarboxylates	Torsion angles [°][a])				
		Θ_1	Θ_2	Θ_3	Θ_4	Θ_5
11	$R^1 = R^3 = H$, $R^2 = Ph$	63.1(3)	65.2(3)	161.4(2)	133.7(2)	– 40.6(3)
		64.8(3)	65.9(3)	– 15.3(3)	136.2(2)	– 41.8(3)
12	$R^1 = Me$, $R^2 = Ph$, $R^3 = H$	67.0(2)	68.2(2)	156.0(6)	135.2(2)	– 39.3(2)
				– 6.6(12)		
14[c])	$R^1 = R^2 = Me$, $R^3 = t$-Bu	63.9(2)	65.7(2)	– 14.1(2)	130.8(2)	– 33.0(2)
15[d])		63.0(1)	66.3(1)	159.2(1)	134.5(1)	– 40.2(1)

[a]) The torsion angles Θ are referring to the (*P*) configuration. $\Theta_1 = \Theta$(C(5)–C(5a)–C(10a)–C(1)); $\Theta_2 = \Theta$(C(6)–C(5a)–C(10a)–C(10)); $\Theta_3 = \Theta$(O=C–C(4)–C(3)); $\Theta_4 = \Theta$(O=C–C(5)–C(5a)); $\Theta_5 = \Theta$(MeOOC–C(4)–C(5)–COOMe). Values in the second line refer to the corresponding s-*cis* conformations of MeOOC–C(4). [c]) Data taken from [3]. [d]) Data taken from [8]; torsion angles correspond to those defined under [b]).

whereas the other molecule represents almost a perfect s-*cis*-conformation (*Table 1*). It is quite interesting to note that the MeOCO group at C(5) occupies a position close to a s-*trans*-conformation in both molecules. This is also true for other heptalenedicarboxylates such as **14** and **15** (*Table 1*) which carry substituents at the *peri*-positions, but may crystallize with MeOCO–C(4) in s-*cis* (**14**) or s-*trans* conformation (**15**).

The asymmetric unit of the crystals of **12** contains one molecule in which the MeOCO group at C(4) is disordered over two orientations, which again can be assigned to a major s-*trans* (*ca.* 65%) and a minor s-*cis*-conformation (see *Fig. 3*). The torsion angles at the ester groups are close to those of **11** and of other heptalenedicarboxylates (*Table 1*).

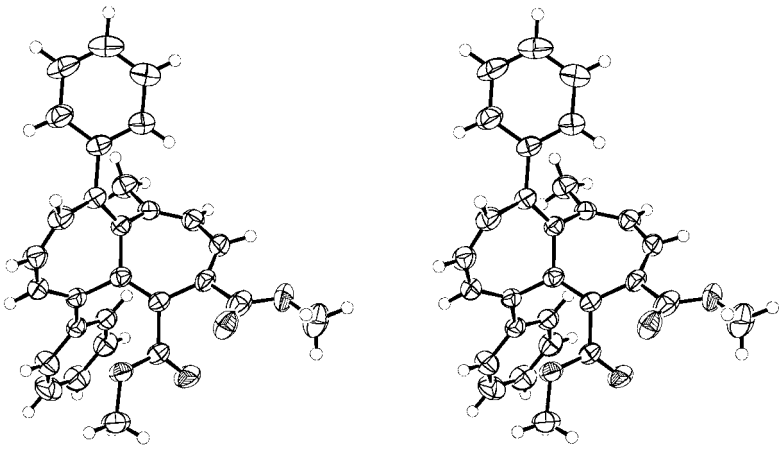


Fig. 3. *Stereoscopic view of the X-ray crystal structure of dimethyl 1-methyl-6,10-diphenylheptalene-4,5-dicarboxylate* (**12**; the s-*trans* conformation of MeOCO–C(4) in the (*P*) configuration of the heptalene skeleton is shown)

One can assume that the conformation at the ester groups will not change very much in solution, that means that the MeOCO group at C(5) is almost perfectly shielded against a nucleophilic attack at its C=O group, so that all primary nucleophilic attacks occur at the C=O group at C(4), which has always been observed by us.

We thank Dr. *L. Bigler* and his group 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 [4][5].

1. *Syntheses of Azulenes*. 1.1. *Attempted Synthesis of 4,6,8-Triphenylazulene*. The reaction was performed in analogy to [2]. 2,4,6-Triphenyl pyrylium tetrafluoroborate (*AVOCADO Research Chemicals Ltd.*) (200 mg, 0.50 mmol) was reacted with freshly prepared cyclopentadiene (0.06 ml, 0.75 mmol) and NaH (30 mg, 0.75 mmol) in DMF (20 ml) at 150° during 24 h. After normal workup, 4,6,8-triphenylazulene was not detectable.

1.2. *4,8-Diphenylazulene-1-carbaldehyde* (**4**). $POCl_3$ (15 ml, 165 mmol) was dropped to DMF (20 ml) under stirring at 0° within 10 min. This *Vilsmeier* reagent was introduced slowly into a soln. of **1** (4.00 g, 14.3 mmol) in DMF (50 ml) at 0°. After addition, the temp. was raised to 25°, and stirring was continued for 30 min. Then, the

red mixture was poured into ice-water, and 2M NaOH (100 ml) was added. Extraction with Et_2O and CC (silica gel; hexane/Et_2O 1:2) yielded **4** (3.06 g, 70%) as violet crystals. M.p. 161–162° (hexane/Et_2O). R_f (hexane/Et_2O 1:2) 0.42. IR (KBr): 3421*w*, 3050*w*, 1690*w*, 1636*s*, 1566*m*, 1491*m*, 1456*m*, 1440*m*, 1429*m*, 1350*m*, 1329*m*, 1291*w*, 1225*m*, 1209*m*, 1157*w*, 1066*w*, 1055*w*, 1024*w*, 934*w*, 904*w*, 850*w*, 816*w*, 793*m*, 759*m*, 746*m*, 702*s*, 646*w*, 594*w*, 516*w*, 477*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.80 (*s*, CHO); 8.26 (*d*, ^3J = 4.5, H–C(2)); 7.35 (*t*, ^2J = 10.3, H–C(6)); 7.59–7.42 (*m*, 10 arom. H, H–C(5), H–C(7)); 7.13 (*d*, ^3J = 4.5, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 189.17 (*d*, CHO); 153.09, 151.57, 145.32 (3*s*), 137.94, 135.90, 129.85, 129.40 (4*d*), 129.00, 116.97, 116.48, 116.16 (4 *d*, each 2 arom. C); 120.62 (*d*). EI-MS: 309 (24, $[M+1]^+$), 308 (100, $M^{+\cdot}$), 307 (32), 294 (11), 294 (8), 291 (8), 169 (9), 160 (21), 279 (26), 278 (15), 277 (14), 276 (18), 232 (29), 231 (31), 215 (12), 203 (18), 202 (40), 201 (9), 200 (9), 157 (11), 116 (12), 105 (13), 86 (9), 77 (8), 58 (18), 43 (22), 41 (8). Anal. calc. for $C_{23}H_{16}O$ (308.37): C 89.58, H 5.23; found: C 89.54, H 5.30.

1.3. *1-Methyl-4,8-diphenylazulene* (**6**). Aldehyde **4** (1.74 g, 5.6 mmol) in 100 ml diglyme/Et_2O 1:1 and $BF_3 \cdot OEt_2$ (3 ml, 22.4 mmol) in Et_2O (20 ml) were added drop by drop to a soln. of $NaBH_4$ (0.635 g, 16.8 mmol) in diglyme (100 ml) at 0° within 2 h. After addition, the stirring was continued for 1 h, and, then, this mixture was poured into ice-water. Extraction by hexane and CC (alumina; hexane) gave pure **6** (0.92 g, 55%) as blue crystals. M.p. 144–145° (hexane). UV (hexane, $c = 0.493 \times 10^{-4}$ M)[4]): λ_{max} 243 (4.31), 264 (4.54), 354 (3.55); λ_{min} 224 (4.16), 250 (4.16), 331 (3.38). IR (KBr): 3424*w*, 3051*w*, 3024*w*, 2922*w*, 1659*w*, 1954*w*, 1551*m*, 1515*m*, 1491*m*, 1457*s*, 1439*m*, 1416*m*, 1267*w*, 1218*w*, 1200*w*, 1167*w*, 1074*m*, 1025*w*, 1005*m*, 956*w*, 925*w*, 901*w*, 843*w*, 815*w*, 798*m*, 783*m*, 755*s*, 735*m*, 701*s*, 623*w*, 530*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51–7.46 (*m*, 2 arom. H, H–C(2)); 7.44–7.31 (*m*, 8 arom. H, H–C(6)); 6.98 (*d*, ^3J = 4.0, H–C(3)); 7.02 (*d*, ^3J = 10.2, H–C(7)); 6.95 (*d*, ^3J = 10.3, H–C(5)); 1.75 (*s*, Me–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.88, 149.95, 145.12, 144.34, 140.06 (5*d*), 139.82, 134.33, 129.01, 116.88 (4*d*), 116.33, 127.93, 127.62, 127.52, 127.26, 125.29, 124.06, 118.67 (7*d*); 17.13 (*q*). EI-MS: 295 (25, $[M+1]^+$), 294 (100, $M^{+\cdot}$), 293 (24), 169 (7), 279 (12), 278 (14), 277 (8), 276 (10), 230 (9), 218 (10), 217 (16), 215 (19), 202 (12), 154 (16), 139 (7), 138 (7), 91 (10), 44 (8), 43 (14), 32 (30). Anal. calc. for $C_{23}H_{18}$ (294.14): C 93.84, H 6.16; found: C 93.78, H 6.16.

1.4. *6-Methyl-4,8-diphenylazulene* (**2**) *and 1,6-Dihydro-6-methyl-4,8-diphenylazulene* (**3**). Azulene **2** was prepared according to [5]. When the mixture was purified by CC (silica gel; hexane), in addition to main product **2**, a small fraction of **3** was collected, which slowly crystallized from hexane/Et_2O as orange crystals. Pure **3**, on the treatment with chloranil (= 2,3,5,6-tetrachlorobenzo-1,4-quinone) at 40° in Et_2O for 5 h, gave **2** in quantitative yield.

Data of **2**: M.p. 156–157° (hexane; [5]: blue oil). R_f (hexane) 0.48. UV (hexane, $c = 0.648 \times 10^{-4}$ M)[4]): λ_{max} 238 (4.31), 267 (4.60), 351 (3.52); λ_{min} 219 (4.18), 247 (4.26), 327 (3.38). IR (KBr): 3423*w*, 3052*w*, 3022*w*, 2923*m*, 1653*w*, 1953*w*, 1637*w*, 1565*m*, 1550*m*, 1479*m*, 1456*m*, 1443*m*, 1434*s*, 1322*w*, 1270*w*, 1218*m*, 1071*m*, 1024*m*, 999*m*, 851*w*, 835*w*, 769*s*, 751*s*, 716*m*, 689*s*, 654*w*, 516*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.63–7.59 (*m*, 4 arom. H, H–C(2)); 7.53–7.45 (*m*, 6 arom. H); 7.01 (*s*, H–C(5), H–C(7)); 7.06 (*d*, ^3J = 3.9, H–C(1), H–C(3)); 2.67 (*s*, Me–C(6)). EI-MS: 295 (21, $[M+1]^+$), 294 (82, $M^{+\cdot}$), 293 (16), 161 (24), 160 (100), 279 (66), 278 (35), 277 (26), 276 (16), 252 (12), 218 (11), 217 (9), 215 (12), 203 (13), 202 (32), 201 (9), 200 (9), 140 (8), 139 (18), 138 (21), 133 (9), 132 (8), 126 (14).

Data of **3**: M.p. 96–97° (hexane/Et_2O). R_f (hexane) 0.62. UV (hexane, $c = 0.679 \times 10^{-4}$ M): λ_{max} 251 (4.42); λ_{min} 216 (4.24). IR (KBr): 3424*w*, 3072*w*, 3032*m*, 3020*m*, 2958*m*, 2924*m*, 1670*w*, 1616*w*, 2738*w*, 1948*w*, 1880*w*, 1807*w*, 1671*w*, 1599*w*, 1573*w*, 1489*m*, 1455*m*, 1443*m*, 1401*w*, 1377*w*, 1340*m*, 1306*w*, 1257*w*, 1235*w*, 1179*w*, 1163*w*, 1141*w*, 1108*w*, 1075*m*, 1041*w*, 1024*w*, 1000*w*, 987*w*, 961*m*, 936*w*, 917*w*, 894*m*, 872*w*, 856*m*, 845*m*, 833*w*, 827*w*, 765*s*, 738*m*, 702*s*, 679*s*, 659*m*, 640*m*, 626*w*, 541*w*, 513*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.25 (*m*, 10 arom. H); 6.59 (*d*, with f.s., ^3J = 5.3, H–C(2)); 6.34 (*d*, with f.s., ^3J = 5.4, H–C(3)); 5.42 (*d*, ^3J = 5.8, H–C(5)); 5.21 (*d*. with f.s., ^3J = 5.7, H–C(7)); 3.61 (*d*, *A* of *AB*, ^2J = 14.4, H_A–C(1)); 3.18 (*d*, *B* of *AB*, ^2J = 14.4, H_B–C(1)); 1.76 (*m*, H–C(6)); 1.47 (*d*, ^3J = 7.0, Me–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.88, 145.01, 142.47, 140.42, 137.13, 135.32 (6*s*); 134.48, 130.54, 116.90, 116.70, 116.00, 126.90, 126.81, 126.45, 126.01 (9*d*); 43.34 (*t*); 33.22 (*d*); 19.58 (*q*, Me–C(6)). EI-MS: 297 (25, $[M+1]^+$), 296 (100, $M^{+\cdot}$), 295 (7), 162 (18), 161 (73), 160 (9), 279 (11), 268 (10), 267 (38), 266 (22), 265 (16), 253 (10), 252 (15), 204 (10), 203 (22), 202 (18), 126 (7), 32 (11). Anal. calc. for $C_{23}H_{20}$ (296.40): C 93.20, H 6.80; found: C 93.21, H 7.01. The structure of **3** was confirmed by X-ray crystal-structure analysis (*cf. Table 2*).

1.5. *6-Methyl-4,8-diphenylazulene-1-carbaldehyde* (**5**). The reaction was performed in analogy to *1.2.* $POCl_3$ (1.5 ml, 165 mmol) was dropped into DMF (10 ml) under stirring at 0° within 10 min. This *Vilsmeier* reagent was

---

[4]) Absorption bands above 400 nm have not been registered.

Table 2. *Crystallographic Data of* **3**, **11**, *and* **12**

		3	**11**	**12**
Empirical formula		$C_{23}H_{20}$	$C_{16}H_{22}O_4$	$C_{29}H_{24}O_4$
Formula weight [g mol^{-1}]		296.41	422.48	436.50
Crystal color, habit		orange, prism	orange, prism	yellow, plate
Crystal dimensions [mm]		$0.15 \times 0.20 \times 0.25$	$0.10 \times 0.15 \times 0.18$	$0.08 \times 0.20 \times 0.20$
Temperature [K]		160(1)	160(1)	250(1)
Crystal system		orthorhombic	triclinic	triclinic
Space group		$Pca2_1$	$P\bar{1}$	$P\bar{1}$
Z		4	4	2
Reflections for cell determination		2790	7576	5183
2θ range for cell determination [°]		4 – 60	4 – 50	4 – 55
Unit-cell parameters:	a [Å]	9.3998(2)	9.8774(1)	10.0117(2)
	b [Å]	10.2111(2)	12.7852(2)	10.7690(2)
	c [Å]	17.4501(3)	19.0973(3)	12.6350(2)
	α [°]	90	92.5045(5)	110.4560(9)
	β [°]	90	102.4708(6)	111.8989(9)
	γ [°]	90	111.825(1)	96.1826(9)
	V [Å^3]	1674.90(6)	2165.47(6)	1138.99(4)
$F(000)$		632	888	460
D_x [g cm^{-3}]		1.175	1.296	1.273
$\mu(\text{Mo}K_\alpha)$ [mm^{-1}]		0.0661	0.0859	0.0839
Scan type		ϕ and ω	ϕ and ω	ϕ and ω
2θ(max) [°]		60	50	55
Total reflections measured		32160	35881	41764
Symmetry independent reflections		4633	7645	5188
R_{int}		0.064	0.072	0.048
Reflections with $I > 2\sigma(I)$		3507	5286	3746
Reflections used in refinement		3507	7645	3746
Parameters refined		208	583	326
R [on F; $I > 2\sigma(I)$ reflections]		0.0444	0.0480	0.0519
wR [on F; $I > 2\sigma(I)$ reflections]		0.0411	–	0.0584
wR [on F^2; all indept. reflections]		–	0.1369	–
Weights: p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$		0.015	[a])	0.005
Goodness-of-fit		1.481	1.074	2.976
Secondary extinction coefficient		$3.4(5) \times 10^{-6}$	0.011(1)	$7.1(9) \times 10^{-6}$
Final $\Delta_{\text{max}}/\sigma$		0.0004	0.001	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]		0.18; −0.16	0.24; −0.22	0.18; −0.19

[a]) $w^{-1} = \sigma^2(F_o)^2 + (0.0535P)^2 + 0.5479P$, where $P = (F_o^2 + 2F_c^2)/3$.

introduced slowly into a soln. of **2** (630 mg, 2.14 mmol) in DMF (10 ml) at 0°. After addition, the temp. was raised to 25°, and stirring was continued for 30 min. Then, the red mixture was poured into ice water, and 2M NaOH (100 ml) was added. Extraction with Et_2O and CC (silica gel; hexane/Et_2O 1:2) yielded **5** (110 mg, 16%). Violet crystals. M.p. 132–133° (Et_2O/hexane). R_f (Et_2O/hexane 4:6) 0.62. IR (KBr): 3423*w*, 3051*w*, 3022*w*, 2923*m*, 1653*w*, 1953*w*, 1637*w*, 1565*m*, 1550*m*, 1479*m*, 1456*m*, 1443*m*, 1434*s*, 1322*w*, 1270*w*, 1218*m*, 1071*m*, 1024*m*, 1024*m*, 999*m*, 850*w*, 835*w*, 769*s*, 751*s*, 716*m*, 689*s*, 654*w*, 516*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.73 (*s*, CHO); 8.21 (*d*, $^3J = 4.5$, H–C(2)); 7.58–7.48 (*m*, 10 arom. H); 7.38 (*s*, H–C(5), H–C(7)); 7.02 (*d*, $^3J = 4.4$, H–C(3)); 2.72 (*s*, Me–C(6)). EI-MS (GC-MS): 323 (25, $[M+1]^+$), 322 (100, $M^{+\cdot}$), 321 (71), 308 (21), 307 (72), 306 (8), 305 (14), 294 (11), 293 (35), 291 (7), 290 (7), 169 (19), 161 (7), 279 (19), 278 (25), 277 (26), 276 (35), 252 (7), 245 (10), 244 (24), 216 (12), 215 (41), 214 (11), 207 (33), 201 (10), 189 (11), 153 (10), 145 (22), 144 (12), 139 (35), 138 (40), 132 (10), 131 (18), 126 (15), 125 (10), 91 (13), 77 (8), 57 (8).

1.6. *1,6-Dimethyl-4,8-diphenylazulene* (**7**). The reaction was performed in analogy to *1.3.* Aldehyde **5** (100 mg, 0.31 mmol) in 20 ml diglyme/Et_2O 1:1 and $BF_3 \cdot OEt_2$ (0.2 ml, 1.50 mmol) in Et_2O (20 ml) were added dropwise to a soln. of $NaBH_4$ (43 mg, 1.14 mmol) in diglyme (20 ml) at 0° within 2 h. After workup, CC (alumina; hexane) gave pure **7** (64 mg, 67%). Blue crystals. **7**: M.p. 112° (hexane). R_f (hexane) 0.5. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51–7.46 (*m*, 2 arom. H); 7.44–7.16 (*m*, 8 arom. H, H–C(2)); 6.87 (*s*, H–C(7)); 6.86 (*d*, ^3J = 4.4, H–C(3)); 6.80 (*s*, H–C(5)); 2.50 (*s*, Me–C(6)); 1.76 (*s*, Me–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.89, 149.03, 145.55, 145.41, 144.76, 138.54 (6*s*); 138.37, 131.97, 116.97, 116.84, 116.44, 127.88, 127.61, 127.17, 126.90, 125.54, 118.81 (11*d*); 16.29 (*q*, *Me*–C(6)); 17.06 (*q*, *Me*–C(1)). EI-MS: 309 (26, $[M+1]^+$), 308 (100, $M^{+\bullet}$), 307 (19), 294 (16), 293 (14), 292 (10), 291 (10), 169 (9), 278 (9), 276 (7), 232 (14), 231 (13), 216 (7), 215 (17), 205 (7), 202 (11), 139 (7), 138 (7), 91 (8), 57 (17), 56 (7), 43 (11), 41 (11), 32 (8).

1.7. *3-Methyl-4,8-diphenylazulene-1-carbaldehyde* (**8**). The reaction was performed in analogy to *1.2.* $POCl_3$ (0.2 ml, 2.2 mmol) was dropped into DMF (2 ml) under stirring at 0° within 10 min. This *Vilsmeier* reagent was introduced slowly into a soln. of **6** (100 mg, 0.34 mmol) in DMF (10 ml) at 0°. After addition, the temperature was raised to 25°, and stirring was continued for 30 min. Then, the red mixture was poured into ice water, and 2M NaOH (20 ml) was added. Extraction with Et_2O and CC (silica gel; hexane/Et_2O 1:2) yielded **8** (50 mg, 45%). Violet crystals. M.p. 150–151° (Et_2O/hexane). IR (KBr): 3393*w*, 2923*m*, 1653*w*, 1722*w*, 1632*s*, 1560*m*, 1520*m*, 1501*m*, 1455*m*, 1424*m*, 1397*m*, 1364*m*, 1353*m*, 1263*w*, 1191*m*, 1071*m*, 1027*w*, 1010*m*, 936*w*, 907*w*, 811*w*, 769*m*, 754*s*, 701*s*, 647*w*, 610*w*, 598*w*, 524*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.64 (*s*, CHO); 8.09 (*s*, H–C(2)); 7.49 (*t*, partly overlapped, ^3J = 10.4, H–C(6)); 7.43–7.37 (*m*, 8 arom. H); 7.34–7.28 (*m*, 2 arom. H); 7.25 (*d*, ^3J = 10.1, H–C(7)); 7.19 (*d*, ^3J = 9.7, H–C(5)); 1.67 (*s*, Me–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 186.84 (*d*, CHO); 153.00, 150.57, 145.74, 144.27 (4*s*); 142.31, 141.08, 139.88 (2*s*); 134.91, 130.12, 129.17 (3*d*); 129.03 (*s*); 116.93, 116.83, 116.73, 116.58 (4*d*); 116.23 (*s*); 127.89 (*d*). EI-MS: 323 (24, $[M+1]^+$), 322 (100, $M^{+\bullet}$), 321 (46), 308 (7), 307 (29), 305 (7), 294 (9), 293 (23), 291 (8), 169 (15), 279 (19), 278 (23), 277 (13), 276 (18), 245 (23), 215 (21), 202 (6), 149 (17), 145 (7), 139 (8), 138 (12), 123 (8), 106 (7), 105 (8), 97 (11), 91 (10), 85 (7), 83 (18), 81 (7), 77 (7), 71 (12), 70 (7), 69 (15), 58 (9), 57 (22), 56 (8), 55 (17), 43 (41), 41 (15), 32 (16). Anal. calc. for $C_{24}H_{18}O$ (322.14): C 89.41, H 5.63; found: C 88.77, H 5.93.

1.8. *1,3-Dimethyl-4,8-diphenylazulene* (**9**). The reaction was performed in analogy to *1.3.* Aldehyde **8** (380 mg, 1.13 mmol) in 30 ml diglyme/Et_2O 1:1 and $BF_3 \cdot OEt_2$ (129 mg, 3.4 mmol) in Et_2O (20 ml) were added dropwise to a soln. of $NaBH_4$ (129 mg, 3.40 mmol) in diglyme (20 ml) at 0° within 2 h. After workup, CC (alumina/hexane) gave pure **9** (50 mg, 14%). Blue crystals. M.p. 100–101°(hexane). R_f (hexane) 0.67. UV (hexane, $c = 0.429 \times 10^{-4}$ M)[4]): λ_{max} 246 (4.32), 262 (4.57), 358 (3.60), 374 (3.45); λ_{min} 216 (4.19), 253 (4.29), 335 (3.39), 370 (3.40). IR (KBr): 3443*w*, 3025*w*, 3024*w*, 2924*w*, 1659*w*, 1947*w*, 1646*w*, 1598*w*, 1563*m*, 1550*s*, 1534*m*, 1489*m*, 1463*m*, 1444*s*, 1266*w*, 1201*w*, 1153*w*, 1071*w*, 1029*w*, 1004*m*, 996*w*, 895*w*, 858*w*, 773*m*, 760*s*, 701*s*, 606*w*, 532*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.16 (*m*, 10 arom. H, H–C(2)); 7.20 (*t*, $^3J(6,7) = {}^3J(5,6) = 10.2$, H–C(6)); 6.73 (*d*, $^3J(7,6) = {}^3J(5,6) = 10.2$, H–C(5), H–C(7)); 1.68 (*s*, Me–C(1)); 1.63 (*s*, Me–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.02, 145.61 (2*s*); 144.86 (*d*); 134.60 (*s*); 134.43, 116.92, 127.62, 127.10 (4*d*); 126.84, 127.26 (2*d*); 124.64 (*d*); 17.08 (*q*). EI-MS: 309 (27, $[M+1]^+$), 308 (100, $M^{+\bullet}$), 307 (8), 296 (8), 294 (10), 293 (17), 292 (8), 291 (11), 169 (8), 278 (8), 276 (6), 230 (9), 215 (13), 202 (6), 139 (7), 138 (8), 57 (13), 55 (5), 43 (8), 41 (6).

2. *Synthesis of Dimethyl Heptalene-4,5-dicarboxylates.* 2.1. *Dimethyl 1-Methyl-6,10-diphenylheptalene-4,5-dicarboxylate* (**12**) and *Dimethyl 3-Methyl-4,8-diphenylazulene-1,2-dicarboxylate* (**16**). Azulene **6** (0.92 g, 3.13 mmol) was dissolved in MeCN (18 ml) in a *Schlenk* vessel and dimethyl acetylenedicarboxylate (ADM; 1.2 ml, 9.84 mmol) was added. The vessel was flushed with Ar and then closed. The blue soln. was stirred during 72 h at 100° while the color of the soln. changed to brownish yellow. The solvent was removed under reduced pressure, and the residue was purified by CC (silica gel; hexane/Et_2O 1:3) to give **12** (0.55 g, 40%) as yellow foam, followed by a blue fraction, which contained **16** in small amounts (<1%). Heptalene **12** could be crystallized from acetone. When the reaction of azulene **6** with ADM was performed in DMF as solvent at 170° during 48 h, the yield of **12** amounted to 22%.

Data of **12**: M.p. 200 – 201° (hexane/Et_2O 1 : 1). R_f (hexane/Et_2O 1:3) 0.45. UV (hexane, $c = 0.333 \times 10^{-4}$ M)[4]): λ_{max} 198 (4.70), 291 (4.37), 385 (sh, 3.24); λ_{min} 272 (4.32). IR (KBr): 3419*w*, 3019*w*, 2994*w*, 2949*w*, 1736*s*, 1718*s*, 1595*w*, 1573*w*, 1552*w*, 1493*w*, 1432*m*, 1368*w*, 1342*w*, 1257*s*, 1216*m*, 1191*m*, 1171*m*, 1137*m*, 1093*w*, 1067*w*, 1052*m*, 1031*m*, 984*w*, 935*w*, 891*w*, 850*w*, 796*m*, 772*m*, 758*s*, 734*m*, 702*m*, 667*w*, 576*w*, 504*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83 (*d*, *J* = 6.0, H–C(3)); 7.47–7.44 (*m*, 2 arom. H); 7.30–7.15 (*m*, 8 arom. H); 6.90 (*d*, ^3J = 6.3, H–C(7)); 6.83 (*dd*, $^3J(8,7) = 6.4$, $^3J(8,9) = 11.2$, H–C(8)); 6.59 (*d*, ^3J = 11.2, H–C(9)); 6.44 (*dd*, *J* = 1.3/6.4, H–C(2)); 3.73 (*s*, MeOC(O)–C(4)); 3.23 (*s*, MeOC(O)–C(5)); 1.61 (*s*, Me–C(1)). ^{1}H-NMR (600 MHz, (D_6)acetone): 7.79 (*dd*, *J* = 0.8, 6.1, H–C(3)); 7.51–7.49 (*m*, 2 arom. H); 7.36–7.34 (*m*, 3 arom. H); 7.16 (*t*-like, 2

arom. H); 7.23 (*d*, ^3J = 7.3, 1 arom. H); 7.21–7.19 (*m*, 2 arom. H); 7.01 (*d*, ^3J = 6.5, H–C(7)); 6.88 (*dd*, ^3J(8,7) = 6.5, ^3J(8,9) = 11.4, H–C(8)); 6.59 (*d*, ^3J = 11.4, H–C(9)); 6.56 (*dd*, *J* = 0.8, 6.1, H–C(2)); 3.67 (*s*, MeO*C*(O)–C(4)); 3.17 (*s*, MeO*C*(O)–C(5)); 1.60 (*s*, Me–C(1)). ^{13}C-NMR (150 MHz, (D_6)acetone): 168.10 (*s*, MeO*C*(O)–C(4)); 167.73 (*s*, MeO*C*(O)–C(5)); 144.85 (*s*, C(5)); 141.62 (*d*, C(3)); 140.67 (*s*, 1 arom. C); 140.48 (*s*, C(5a)); 140.02 (*s*, 1 arom. C); 137.71 (*s*, C(10)); 137.06 (*s*, C(6)); 134.55 (*d*, C(9)); 134.25 (*d*, C(8)); 134.07 (*s*, C(4)); 130.77 (*d*, 2 × enhanced intensity, 2 arom. C); 130.48 (*s*, C(10a)); 130.00 (*d*, C(2)); 129.95 (*d*, 2 × enhanced intensity, 2 arom. C); 129.77 (*d*, 2 × enhanced intensity, 2 arom. C); 129.50 (*d*, 1 arom. C); 116.94 (*d*, 1 arom. C); 116.58 (*s*, C(1)); 127.95 (*d*, 2 × enhanced intensity, 2 arom. C); 126.67 (*d*, C(7)); 52.82 (*q*, *Me*OC(O)–C(4)); 52.21 (*q*, *Me*OC(O)–C(5)); 23.98 (*q*, Me–C(1)). CI-MS: 455 (9, $[M+NH_4]^+$), 454 (29), 439 (5), 438 (9), 437 (29), 436 (6, $M^{+\cdot}$), 422 (6), 415 (6), 414 (20), 407 (7), 406 (30), 405 (100, $[M-OMe]^+$), 343 (13). Anal. calc. for $C_{29}H_{24}O_4$ (436.50): C 79.80, H 5.54; found: C 79.89, H 5.81. The structure of **12** was confirmed by X-ray crystal-structure analysis (*cf. Tables 1* and *2*).

Data of **16**: R_f (hexane/Et_2O 1:3) 0.36. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.70 (*t*, ^3J = 10.3, H–C(6)); 7.57–7.44 (*m*, 10 arom. H); 7.27 (*d*, ^3J = 11.5, H–C(7)); 7.23 (*d*, ^3J = 10.5, H–C(5)); 3.81(*s*, MeOC(O)–C(1)); 3.16(*s*, MeOC(O)–C(2)); 1.53 (*s*, Me–C(3)).

2.1.1. *Irradiation of* **12**. The soln. of **12** in toluene ($c = 2.3 \times 10^{-2}$ M) was irradiated with the lamp of a fluorescent tube (λ_{max} (emiss.): 366/433 nm) overnight. ^{1}H-NMR analysis showed that its DBS isomer **12′** was not observed (limit of detection *ca.* 1%).

2.2. *Dimethyl 1,8-Dimethyl-6,10-diphenylheptalene-4,5-dicarboxylate* (**13**). The reaction was performed in analogy to *2.1*. Azulene **7** (50 mg, 0.16 mmol) was reacted with ADM (0.06 ml, 0.49 mmol) in 5 ml of MeCN yielding **13** (5 mg, 7%) as yellow foam. R_f (hexane/Et_2O 1:1) 0.22. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72 (*d*, ^3J = 5.2, H–C(3)); 7.38–7.31 (*m*, 2 arom. H); 7.21–7.04 (*m*, 8 arom. H); 6.65 (*s*, H–C(7)); 6.33 (*d*, ^3J = 6.0, H–C(2)); 6.29 (*s*, H–C(9)); 3.66 (*s*, MeOC(O)–C(4)); 3.14 (*s*, MeOC(O)–C(5)); 1.97 (*s*, Me–C(8)); 1.52 (*s*, Me–C(1)). EI-MS (GC): 450 (56, $M^{+\cdot}$), 391 (100, $[M-COOMe]^+$), 359 (67), 331 (61), 316 (56), 315 (44), 161 (95), 253 (67).

2.3. *Attempted Synthesis of Dimethyl 1,3-Dimethyl-6,10-diphenylheptalene-4,5-dicarboxylate* (**10**). The reaction was performed in analogy to *2.1*. Azulene **9** (42 mg, 0.14 mmol) was reacted with ADM (0.05 ml, 0.41 mmol) in 10 ml of MeCN. TLC indicated that a number of products were formed. Trace amounts of **10** could be identified on TLC by its correlated R_f value and its pale yellow color.

2.4. *Dimethyl 6,10-Diphenylheptalene-4,5-dicarboxylate* (**11**). The reaction was performed in analogy to *2.1*. Azulene **1** (250 mg, 0.89 mmol) was reacted with ADM (0.33 ml, 2.70 mmol) in 15 ml of MeCN yielding **11** (160 mg, 42%). Red crystals. M.p. 165° (hexane/Et_2O 1:1). R_f (hexane/Et_2O 1:1) 0.20. UV/VIS (hexane, $c = 0.349 \times 10^{-4}$ M): λ_{max} 294 (4.32); λ_{min} 276 (4.29); 400 (sh, 3.22). IR (KBr): 3409*w*, 3057*w*, 3022*w*, 2948*w*, 1730*s*, 1717*s*, 1595*w*, 1574*w*, 1491*w*, 1437*m*, 1404*w*, 1355*w*, 1302*m*, 1268*s*, 1218*m*, 1184*m*, 1116*m*, 1097*m*, 1067*m*, 1027*m*, 976*w*, 915*w*, 892*w*, 853*w*, 823*w*, 799*w*, 784*m*, 766*m*, 742*s*, 699s, 685*m*, 676*m*, 566*w*, 515*w*. ^{1}H-NMR (300 MHz, (D_6)benzene): 7.77 (*d*, ^3J(3,2) = 6.1, H–C(3)); 7.59 (*d*, ^3J = 7.1, 2 arom. H); 7.16–6.97 (*m*, 8 arom. H); 6.63 (*d*, ^3J(7,8) = 5.8, H–C(7)); 6.51 (*dd*, ^3J(8,7) = 6.0, ^3J(8,9) = 11.4, H–C(8)); 6.44 (*d*, ^3J = 11.3, H–C(9)); 5.88 (*dd*, ^3J(2,3) = 6.1, ^3J(2,1) = 10.2, H–C(2)); 5.69 (*d*, ^3J(1,2) = 10.2, H–C(1)); 3.30 (*s*, MeOC(O)–C(4)); 3.07 (*s*, MeOC(O)–C(5)). ^{1}H-NMR (600 MHz, $CDCl_3$, in thermal equilibrium with 7% of its DBS isomer **11′**): 7.72 (*d*, ^3J(3,2) = 6.2, H–C(3)); 7.42 (*d* with f.s., ^3J = 6.3, 2 arom. H); 7.22–7.19 (*m*, 3 arom. H); 7.18–7.16 (*m*, 2 arom. H); 7.11–7.08 (*m*, 1 arom. H); 7.08–7.05 (*m*, 2 arom. H); 6.72–6.68 (*m*, H–C(7), H–C(8)); 6.49–6.46 (*m*, H–C(9)); 6.39 (*dd*, ^3J(2,3) = 6.2, ^3J(2,1) = 10.2, H–C(2)); 5.90 (*d*, ^3J(1,2) = 10.2, H–C(1)); 3.65 (*s*, MeOC(O)–C(4)); 3.12 (*s*, MeOC(O)–C(5)). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.26 (*s*, MeO*C*(O)–C(5)); 167.12 (*s*, MeO*C*(O)–C(4)); 141.77 (*d*, C(3)); 141.38, 139.54, 138.87, 138.80, 135.82 (5*s*); 135.52 (*d*, C(1)); 135.03 (*s*); 133.58 (*d*, C(9)); 133.23 (*d*, C(8)); 130.83 (*d*, C(2)); 130.40 (*d*, 2 × enhanced intensity, 2 arom. C); 116.58 (*d*, 2 × enhanced intensity, 2 arom. C); 116.39 (*s*); 116.18 (*d*, 2 × enhanced intensity, 2 arom. C); 116.07 (*d*, 1 arom. C); 127.55 (*d*, 1 arom. C); 127.34 (*d*, 2 × enhanced intensity, 2 arom. C); 126.52 (*s*); 126.46 (*d*, C(7)); 52.40 (*q*, *Me*OC(O)–C(4)); 51.85 (*q*, *Me*OC(O)–C(5)). EI-MS: 423 (27, $[M+1]^+$), 422 (88, $M^{+\cdot}$), 421 (11), 391 (18), 390 (23), 375 (6), 365 (6), 364 (34), 363 (100, $[M-COOMe]^+$), 363 (24), 362 (57), 361 (9), 349 (13), 348 (7), 347 (12), 336 (6), 332 (15), 331 (52), 330 (6), 329 (6), 320 (10), 305 (16), 304 (55), 303 (91), 302 (93), 301 (22), 300 (29), 291 (6), 290 (9), 169 (23), 167 (8), 160 (15), 279 (15), 278 (11), 277 (10), 276 (18), 274 (7), 239 (7), 227 (5), 226 (14), 215 (5), 203 (5), 202 (14), 201 (5), 165 (6), 152 (13), 151 (54), 150 (22), 149 (12), 145 (17), 144 (6), 138 (12), 137 (7), 105 (8), 43 (5). Anal. calc. for $C_{16}H_{22}O_4$ (422.47): C 79.60, H 5.25; found: C 79.26, H 5.29. The structure of **11** was confirmed by X-ray crystal-structure analysis (*cf. Tables 1* and *2*).

Data of Dimethyl 6,10-Diphenylheptalene-1,2-dicarboxylate (**11′**; partially recognized NMR signals in thermal equilibrium with 93% of its DBS isomer **11**): ^{1}H-NMR (600 MHz, $CDCl_3$): 5.76 (*d*, ^3J(5,4) = 6.1,

H–C(5)); 3.71 (*s*, MeOC(O)–C(2)); 3.15 (*s*, MeOC(O)–C(1)). ^{13}C-NMR (150 MHz, $CDCl_3$): 167.26 (*s*, *Me*OC(O)–C(5)); 52.80 (*q*, *Me*OC(O)–C(2)); 52.15 (*q*, *Me*OC(O)–C(1)).

3. *X-Ray Crystal-Structure Determination of Compounds* **3**, **11**, *and* **12** (*Tables 1,* and *2* and *Figs. 1–3*)[5]). – All measurements were conducted on a *Nonius KappaCCD* area detector diffractometer [9] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream-700* cooler. The data collection and refinement parameters are given in *Table 2*, while views of the molecules are shown in *Figs. 1–3*. Data reduction was performed with HKL DENZO and SCALEPACK [10]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections, other than the *Friedel* pairs in **3**, were merged. Each structure was solved by direct methods using SIR92 [11], which revealed the positions of all non-H-atoms and the non-H-atoms were refined anisotropically.

The molecule in **3** has pseudo C_s symmetry. The atomic coordinates were tested carefully for a relationship from a higher symmetry space group using the program PLATON [12], but none could be found. Three electron-density peaks were found near each of C(1) and C(3). These peaks corresponded with the positions expected if the parent C-atoms were made up from the contributions from disordered CH_2 and sp^2 CH. Therefore, each of these peaks was assigned as an H-atom with a site-occupation factor of 0.5. A test refinement of the positions of these H-atoms showed that they behaved well. For **12**, the ester substituent at C(4) is disordered with the C=O O-atom and the MeO group occupying two orientations, which differ by a rotation of *ca.* 180° about the C(4)–C(=O) bond. The best results were obtained when the site-occupation factors of the two conformations were set to 0.65 and 0.35, resp. In the case of **11**, there are two symmetry-independent molecules in the asymmetric unit. Their conformations differ by a significant rotation of one of the ester substituents. All of the H-atoms in the structures were placed in geometrically calc. positions and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups of **11**).

The structures of **3**, and **12** were refined on *F* using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. For **11**, the refinement was carried out on F^2 by minimizing the corresponding function based on F^2. Corrections for secondary extinction were applied. For **3** and **12**, one and five low angle reflections, resp., were omitted from the final refinement of each structure because the observed intensities of these reflections were much lower than the calc. values as a result of being partially obscured by the beam stop. Neutral-atom-scattering factors for non-H-atoms were taken from [13a], and the scattering factors for H-atoms were taken from [14]. Anomalous dispersion effects were included in F_c [15]; the values for f' and f'' were those of [13b]. The values of the mass attenuation coefficients were those of [13c]. All calculations for **11** were performed using SHELXL97 [16], while the teXsan crystallographic software package [17] was used for the remaining structures. The crystallographic diagrams were drawn using ORTEPII [18].

REFERENCES

[1] P. Mohler, A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **2000**, *83*, 258.
[2] K. Hafner, H. Kaiser, *Liebigs Ann. Chem*. **1958**, *618*, 140; K. Hafner, H. Kaiser, *Org. Synth.* **1973**, *5*, 1088.
[3] G. Singh, A. Linden, K. Abou-Hadeed, H.-J. Hansen, *Helv. Chim. Acta* **2002**, *85*, 27.
[4] K. Hafner, H. Weldes, *Liebigs Ann. Chem*. **1957**, *606*, 90.
[5] K. Hafner, C. Bernhard, R. Mueller, *Liebigs Ann. Chem*. **1961**, *650*, 35.
[6] L.-F. Tietze, T. Eicher, 'Reaktionen und Synthesen im organisch chemischen Praktikum', Georg Thieme Verlag, Stuttgart, New York, 1981.
[7] A. G. Anderson Jr., R. D. Breazeale, *J. Org. Chem*. **1959**, *625*, 108.
[8] A. Linden, M. Meyer, P. Mohler, A. J. Rippert, H.-J. Hansen, *Helv. Chim. Acta* **1999**, *82*, 2274.
[9] R. Hooft, KappaCCD Collect Software, *Nonius BV*, Delft, The Netherlands, 1999.
[10] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.
[11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.

---

[5]) CCDC-219128–219130 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

[12] A. L. Spek, PLATON, Program for the Analysis of Molecular Geometry, University of Utrecht, The Netherlands, 2001.
[13] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, p. 200.; c) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, p. 219.
[14] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[15] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[16] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[17] teXsan: Single Crystal Structure Analysis Software, Version 1.10, *Molecular Structure Corporation*, The Woodlands, Texas, 1999.
[18] C. K. Johnson, ORTEPII, Report ORNL-5138, *Oak Ridge National Laboratory*, Oak Ridge, Tennessee, 1976.

Received December 14, 2004