Synthesis and Stereochemical Aspects of Ethyl 1,1a,2,3,4,5,6,6a-Octahydro-4-octylcyclopropa[*f*]indene-1-carboxylate

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A novel approach for the synthesis of carbene adducts **9a**/**9b** and **10**/**11** is reported. Identification of the geometric and positional isomers of carbene addition was carried out by reversed-phase HPLC, and the establishment of the structure and configuration of **9a**/**9b** was performed by means of 2D-NMR.

Introduction. – The liquid crystals used in modern display devices are calamitic liquid crystals. A huge number of such liquid crystals have been synthesized and used in practical displays [1][2]. It is known that by modification of the basic structures of liquid-crystal molecules, a wide range of property changes affecting the liquid-crystal behavior of the materials can be produced. The core unit presently used in most of the calamitic liquid crystals is cyclohexane, phenylcyclohexane, *etc*. Therefore, various modifications in the basic cyclohexane, bicyclohexyl and phenylbicyclohexyl structures have been made recently to overcome problems of electrooptic and viscoelastic parameters [3][4].

We developed a completely new core unit – the perhydroazulene unit [5]. It is flat and allows introduction of numerous substituents and its configuration can be affected by the central junction as well as by the relative orientation of the substituents. The key step in the synthesis of such core units is the carbene addition to the C=C bond of the *Birch*-reduction product of appropriate indane (=2,3-dihydro-1*H*-indene) derivatives and subsequent isolation of a single isomer. Our studies on similar compounds indicated that exclusive formation of only one stereoisomer from carbene addition is rarely observed. We now isolated two geometric isomers **9a**/**9b** (carbene addition to the peripheral C=C bond of the cyclohexa-1,4-diene moiety of the *Birch*-reduction product) and their two positional isomers **10**/**11** (carbene addition to the corresponding fusion-site C=C bond).

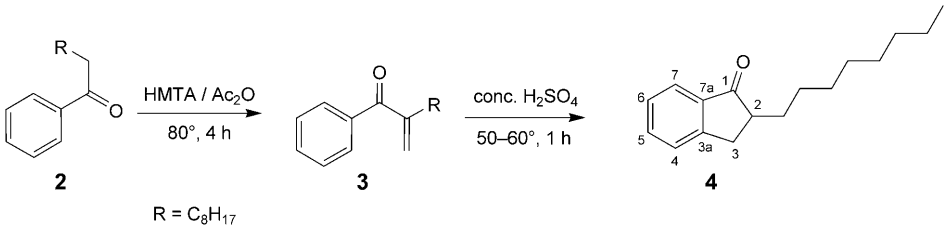
Keehn et al. [6] reported the synthesis of a similar mixture of carbene adducts where they used a fractional-distillation method to separate a 4:1 mixture of two positional isomers. However, nothing was mentioned about the formation and separation of geometric isomers. *Lightner et al.* [7] reported similar carbene-addition reactions where they could separate one major isomer in 45% yield. But they did not report any details about the formation and separation of other isomers or what happened with the remainder 55% of the starting material, a corresponding *Birch*-reduction product.

The structure of the isomer was only elucidated by spectroscopic means and with uncertainty concerning its configuration.

To ensure the quality of our synthetic target which is a key raw material in the synthesis of a variety of new potential mesomorphic materials, a method was needed to separate the mixture **9**/**10**/**11** to proceed with a single isomer of interest. Therefore, we investigated whether reversed-phase HPLC could be used to separate such a mixture of isomers. This allowed the isolation and determination of the relative configuration of the carbene adducts **9a**,**b** and **10**. Furthermore, we applied a DFT method to calculate the coupling constants and to understand the salient features of the isomers.

Results and Discussion. – Our synthetic route started from 2-octylindan-1-one (**4**) which was prepared by a *Mannich*-type reaction from commercially available **2** (*Scheme 1*). There are many reports [8] of the synthetic utility of the *Mannich* reaction for the preparation of 2-alkylindan-1-ones. However, due to an often lengthy procedure and poor yields, we used the procedure of *Bhattacharya et al.* [9] which employs hexamethylenetetramine (HMTA = urotropine = 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) in the presence of Ac_2O as source for the *Mannich* electrophile, resulting in a simple procedure with satisfactory yields. Aqueous workup yielded the propenone **3** which was not isolated but directly subjected to the acid-catalyzed cyclization (H_2SO_4, 50–60°) to produce the corresponding indanone **4** in good yield (69%).

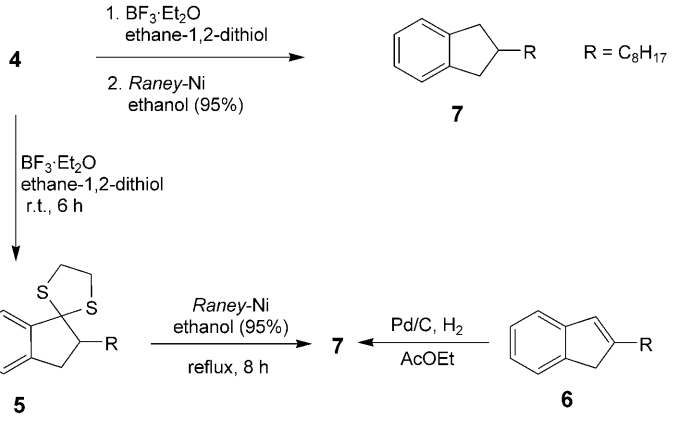
Scheme 1. *Preparation of the Aromatic Ketone* **4**



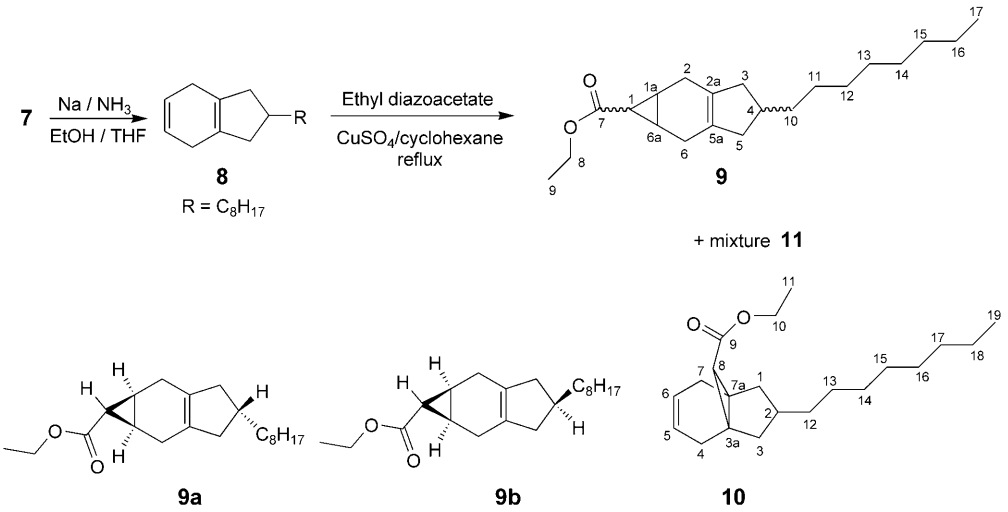
In the next step, the carbonyl group of **4** was reduced to give the hydrocarbon **7** (*Scheme 2*). At first, the *Clemmensen* reduction with amalgamated Zn or catalytic reduction [10] with H_2 in the presence of acid was tried, but both procedures resulted in poor yields (*ca.* 10–20%). Finally, the procedure of *Mitra et al.* [11] was employed where the carbonyl group is first protected as thioketal **5** by reaction with ethane-1,2-dithiol in the presence of $BF_3 \cdot Et_2O$ for 6 h at room temperature. Reductive desulfuration with *Raney*-Ni in EtOH then yielded the desired **7**. Sometimes in addition to **7**, the indene derivative **6** (yield *ca.* 15–20%) was also produced, but by catalytic hydrogenation in the presence of Pd/C, it was converted to **7** in quantitative yield.

Birch reduction [12] of 2-octylindane (**7**) was carried out in liquid ammonia in the presence of Na metal in dry EtOH and THF to provide the 2-octyl-4,7-dihydroindane derivative **8** in 93% yield (*Scheme 3*). It is important to note that **8** was not stable at room temperature and was slowly dehydrogenated by air to **7**. So it was immediately used for further reactions. Continuing the synthesis, **8** was treated with ethyl diazoacetate [13] and a copper catalyst ($CuSO_4$) in refluxing cyclohexane to afford a mixture of carbene adducts **9**/**10**/**11** in acceptable yield (56%). The addition of ethyl diazoacetate

Scheme 2. *Preparation of 2-Octylindane* (**7**)



Scheme 3. *Synthetic Route to* **9a**/**9b**/**10**. Arbitrary atom numbering of the side chains.



to the refluxing mixture of **8** in anhydrous cyclohexane and the copper catalyst resulted in higher yields when the time of addition was prolonged. The adduct mixture **9**/**10**/**11** obtained as a colorless liquid whose NMR data showed the presence of overlapping signals for most of the H- and C-atoms, as expected for such a mixture.

It is worth noting that theoretically one should expect the formation of 8 isomers in the carbene addition of ethyl diazoacetate to a 1,4-diene of type **8** since the addition can proceed either at the peripheral or the fusion-site C=C bond, and in both cases, either as '*exo*'- or '*endo*'-isomers can be formed, '*exo*'/'*endo*' referring to the position of the ester moiety relative to the substituent at the fused 5-membered ring. However, gas-chromatographic analysis of the adduct mixture **9**/**10**/**11** revealed the presence of isomers **9a** (26%), **9b** (21%), **10** (20%), and **11** (6%). Preferential formation of the '*exo*'-isomers suggests that the reaction is either nonconcerted or controlled by steric

effects. After confirmation of the molecular masses of the isomers **9–11** by GC/MS, anal. HPLC was carried out. The HPLC trace (*Fig. 1*) indicated again the presence of **9a** (27%), **9b** (18%), **10** (6%), and **11** (8%) in the carben-addition mixture. Further investigation of the peak due to **11** revealed that **11** was itself a mixture of three isomers with fragmentation patterns in the GC/MS similar to that of **10**. However, due to the very small amounts and less importance for our further studies, a further separation of mixture **11** to establish the relative configuration of each isomer was not carried out.

As the UV data of the isomers **9**–**11** showed similar absorption bands (207 nm), these could not be used as an identification tool during separation. Thus, the fractions obtained by anal. HPLC under optimized conditions were analyzed in detail by GC/MS, allowing to identify the isomer **9b** (t_R 9.12 min; cf. *Fig. 1* for details) and **9a** (t_R 9.67 min) by their MS fragmentation pattern. The isomer **10** (t_R 5.87 min) showed a different fragmentation pattern in comparison to **9a** and **9b**. On this basis, a prep. HPLC separation was carried out within less than 40 min (see *Fig. 2*), the precision of the separation method being assessed by the degree of repeatability of the retention times in a series of injections during a single session. The purities of the thus isolated compounds were determined by GC to be 99% for isomer **10**, 93% for **9a**, and 98% for **9b**. A further refinement of the HPLC parameters (pure MeCN as mobile phase) allowed the separation of 97% pure **9a** and 99% pure **9b**, but the baseline separation for isomers **10** (95% pure) and **11** was lost. Consequently, prep. HPLC separations were performed in two stages, first with the eluent MeCN/MeOH 60:40 (*v*/*v*) then changing to pure MeCN. The method provided a satisfactory separation of **9a** and **9b**, the most important geometric isomers for the use as building blocks of mesogenic materials, showed good sensitivity, recovery, and reproducibility, and allowed, the isolation of the isomers from many grams of carben-addition mixtures, even in the absence of GC/MS.

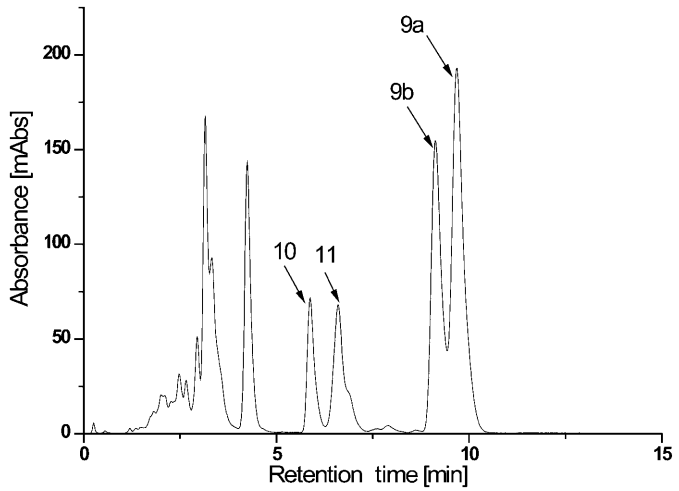


Fig. 1. *Reversed-phase anal. HPLC separation of the mixture of geometric and positional isomers* **9**–**11** *obtained from the cyclopropanation reaction of* **8**. Conditions: *Lichrospher-100-RP18* column (5 μ, 125×4.6 mm); detection at 210 nm; eluent MeOH/MeCN 40:60 (*v*/*v*); flow rate, 0.8 ml min^{-1}.

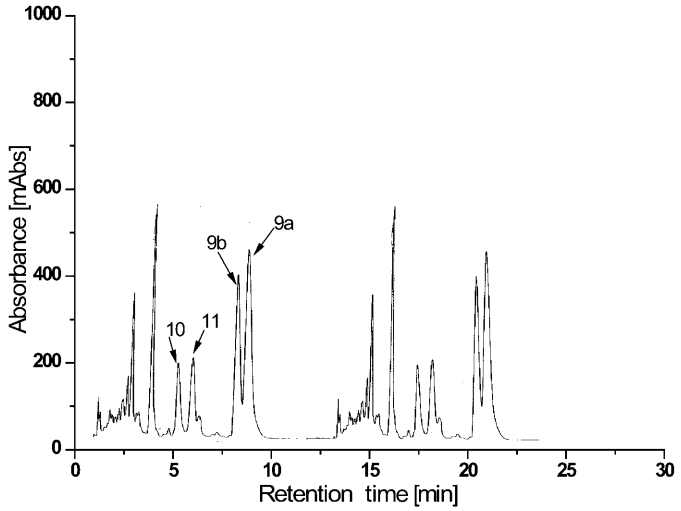


Fig. 2. *Reversed-phase prep. HPLC separation of the mixture of geometric and positional isomers* **9**–**11** *obtained from the carbene reaction.* Conditions: *Lichrospher-100-RP18* column (5 μ, 250×21 mm); detection at 210 nm; eluent MeOH/MeCN 40:60 (*v*/*v*); flow rate, 8 ml min^{-1}. Two repetitive injections are shown.

The structure elucidation of the isomers **9a**,**b** and **10** was carried out by 1D- and 2D-NMR spectroscopy. Most ^{13}C-NMR signals could be assigned by HMQC, and their multiplicities were established by DEPT. For quaternary C-atoms, analysis of HMBC data was sufficient to complete the assignment. Regarding the configuration of **9a**,**b**, the ^{3}J(H,H) and ^{2}J(H,H) values provided clues to the relative position of the H atoms at C(3) and C(5). The methylene groups carry pairwise enantiotopic and diastereotopic H-atoms, enantiotopic with respect to left and right of the internal mirror plane, diastereotopic with respect to above and below the plane of the molecules, perpendicular to the mirror plane. The complete set of NMR data (see *Table*) established the relative configuration of stereoisomers **9a**, **9b**, and **10** which are in good agreement with the single-crystal X-ray structures of similar compounds [14][15] and natural products with a similar skeleton [16].

The ^{1}H-NMR spectra show a *t* at δ 1.40 for **9a** and 1.36 for **9b** with almost the same coupling constant (4.3 Hz) for the H-atoms at the cyclopropane moiety indicating an '*anti*'-relation between the ethoxycarbonyl group and the cyclohexene ring. However, in case of **10** the single cyclopropane H-atom appears as a broad singlet at 1.62. It is worth noting that in **10**, a difference in the geminal *J* of CH_2(4) and CH_2(7) of *ca.* 2 Hz indicates the '*endo*'-position of the ester group at C(8) with respect to the cyclopentane ring. A comparison of the δ(C) of C(2a) and C(5a) of **9a** (δ 129.0) and of **9b** (δ 129.0) with that of C(3a) and C(7a) of **10** (δ 32.68) indicates the formation of isomer **10** where carbene addition took place at the fusion-site C=C bond of **8**.

The most differentiating NMR signals of these isomers are those of the CH_2 groups of the cyclopentane moiety. In case of **9a**, CH_2(3) and CH_2(5) give 2*dd* at δ 1.84 (J = 5.8, 14.2 Hz) and 2.12 (J = 6.4, 14.2 Hz), while in case of **9b** these *dd* appear at δ 1.76 (J = 6.9, 14.4 Hz) and 2.11 (J = 6.7, 14.4 Hz). In case of isomer **10**, CH_2(1) and CH_2(3) again give

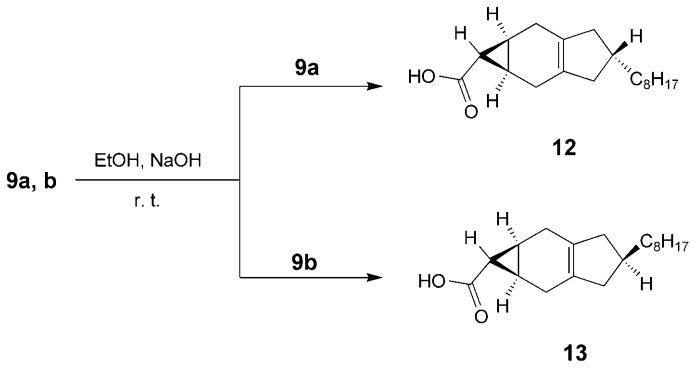
Table. *[1]H-NMR* (400.1 MHz) *and [13]C-NMR* (100.6 MHz) *Data* ($CDCl_3$) *of Compounds* **9a**, **9b**, *and* **10**. δ in ppm, J in Hz. Arbitrary atom numbering (see *Scheme 3*).

	9a		**9b**		**10**	
	^{13}C-NMR	^{1}H-NMR (HMQC)	^{13}C-NMR	^{1}H-NMR (HMQC)	^{13}C-NMR	^{1}H-NMR (HMQC)
H–C(1) or CH_2(1)	23.4	1.40 (*t*, J = 4.3)	23.5	1.36 (*t*, J = 4.3)	40.6	2.28 (*dd*, $J(1\alpha,2)$ = 7.7, $J(1\alpha,1\beta)$ = 12.7, H_α) 1.55 (*dd*, $J(1\beta,2)$ = 7.6, $J(1\beta,1\alpha)$ = 12.7, H_β)
H–C(1a)	22.3	1.71 (br. *s*)	22.3	1.72 (br. *s*)	–	–
CH_2(2) or H–C(2)	24.2	2.26 (br. *s*)	24.2	2.30 (br. *s*)	36.2	1.52 (*m*)
C(2a)	129.0	–	129.0	–	–	–
CH_2(3)	42.5	2.12 (*dd*, $J(3\alpha,4)$ = 6.4, $J(3\alpha,3\beta)$ = 14.2, H_α) 1.84 (*dd*, $J(3\beta,4)$ = 5.8, $J(3\beta,3\alpha)$ = 14.2, H_β)	42.5	2.11 (*dd*, $J(3\alpha,4)$ = 6.7, $J(3\alpha,3\beta)$ = 14.4, H_α) 1.76 (*dd*, $J(3\beta,4)$ = 6.9, $J(3\beta,3\alpha)$ = 14.4, H_β)	40.6	see CH_2(1)
C(3a)	–	–	–	–	32.7	–
H–C(4) or CH_2(4)	36.3	2.11 (*m*)	35.8	2.10 (*m*)	30.1	2.51 (*d*, $J(4\alpha,4\beta)$ = 18.0)
CH_2(5) or H–C(5)	42.5	see CH_2(3)	42.5	see CH_2 (3)	123.7	5.48 (br. *s*)
C(5a)	129.0	–	129.0	–	–	–
CH_2(6) or H–C(6)	24.2	2.26 (br. *s*)	24.2	2.30 (br. *s*)	123.7	5.48 (br. *s*)
H–C(6a)	22.3	1.71 (br. *s*)	22.3	1.72 (br. *s*)	–	–
C(7) or CH_2(7)	175.0	–	175.0	–	30.1	2.11 (*d*, $J(7\alpha,7\beta)$ = 15.9)
C(7a)	–	–	–	–	32.7	–
CH_2(8) or H–C(8)	60.2	4.10 (*q*, J = 7.1)	60.2	4.10 (*q*, J = 7.1)	28.6	1.62 (br. *s*)
Me(9) or C(9)	14.1	1.22 (*t*, J = 7.1)	14.1	1.23 (*t*, J = 7.1)	172.0	–
CH_2(10)	36.8	1.23 (br. *s*)	37.0	1.23 (br. *s*)	60.1	4.08 (*q*, J = 7.1)
CH_2(11) or Me(11)	28.3		28.2		14.1	1.22 (*t*, J = 7.1)
CH_2(12)	29.3		29.3		37.8	1.23 (br. *s*)
CH_2(13)	29.6		29.7		28.7	
CH_2(14)	29.8		29.8		29.3	
CH_2(15)	31.9		32.0		29.6	
CH_2(16)	22.7		22.7		29.8	
Me(17) or CH_2(17)	14.3	0.85 (*t*, J = 6.8)	14.3	0.86 (*t*, J = 6.8)	32.0	
CH_2(18)	–	–	–	–	22.7	
Me(19)	–	–	–	–	14.3	0.85 (*t*, J = 6.6)

rise to 2*dd* at δ 1.55 (J = 7.6, 12.7 Hz) and 2.28 (J = 7.7, 12.7 Hz). Furthermore, the CH_2 (7) and CH_2(4) of the cyclohexene ring of **10** appear as 2 broad *d* at δ 2.11 (^2J = 15.9 Hz) and 2.51 (^2J = 18.0 Hz) with a geminal coupling and small couplings with H−C(5) and H−C(6) and especially with H−C(8), which further indicates the formation of isomer **10**.

To further investigate the relative configuration of the esters **9a** and **9b**, their hydrolysis [17] was carried out in EtOH in the presence of NaOH with a view to subject the resulting acids to X-ray analysis. The obtained acids **12** and **13** (*Scheme 4*) were recrystallized from hexane and CH_2Cl_2 to get single crystals. However, the quality of the obtained crystals in both cases was not good enough for the X-ray analysis. The NMR data of compounds **12** and **13** further justified the retention of configuration.

Scheme 4. *Synthetic Route to* **12/13**



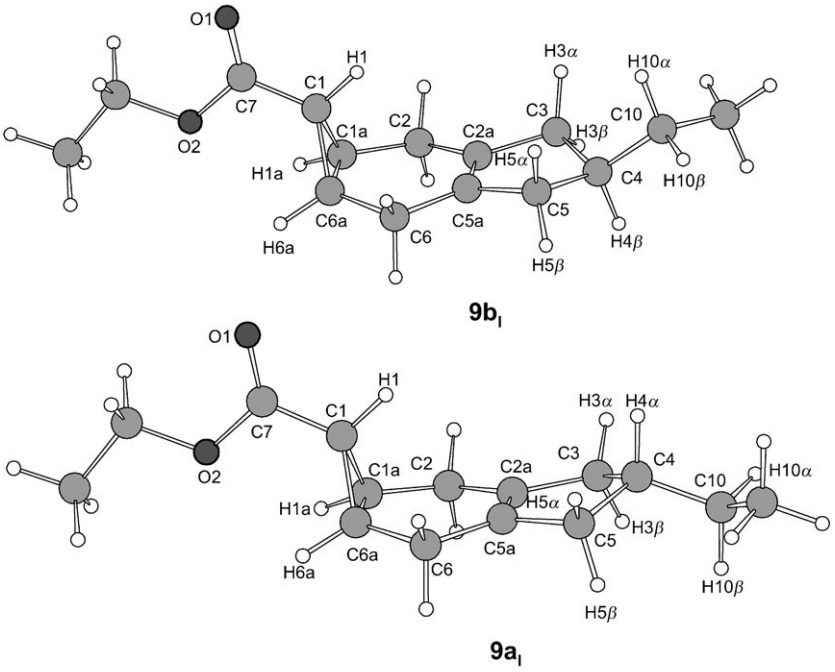


Fig. 3. *B3LYP/6-31+G** optimized model structures* $\mathbf{9a_1}$ *and* $\mathbf{9b_1}$ *with a 4-ethyl group instead of the 4-octyl group*

In the NMR spectra of **12** and **13**, again a *t* at δ 1.44 (**12**) and 1.38 (**13**) with almost the same coupling constant (4.2 Hz) for the H-atoms at the cyclopropane moiety is observed which further indicates the retention of the '*anti*'-relation between the carboxy group and the cyclohexene ring. Furthermore, in case of **12**, the CH_2 groups of the cyclopentane moiety $CH_2(3)$ and $CH_2(5)$, give again 2*dd* at δ 1.87 (J = 5.8, 13.2 Hz) and 2.25 (J = 8.3, 13.2 Hz), while in case of **13** these *dd* appear at δ 1.75 (J = 5.8, 15.1 Hz) and 2.35 (J = 6.6, 15.1 Hz).

We have also calculated the energy-minimized model structures **9a$_1$** and **9b$_1$** with a 4-ethyl instead of the 4-octyl group (*Fig. 3*). These model structures show the alkyl substituent at C(4), as expected, in a pseudoequatorial position of the envelop conformation of the cyclopentane ring.

Conclusions. – The results of this study establish the relative configurations of the carbene adducts **9a**,**b** and **10** which are potential mesogenic materials. These geometric as well as positional isomers can be separated by reversed-phase HPLC. Complete analysis of the NMR data confirm their configuration. This new approach to separate and characterize various isomers obtained by carbene addition will be the subject of future developments in the area of liquid crystals.

Experimental Part

General. All org. solvents were HPLC grade and purchased from *Baker GmbH*, Germany, and the H_2O was deionized water purified by a *Millipore* deionization device (Milford, MA, USA). The Ar gas was of high-purity grade. TLC: *PolyGram Sil G/UV$_{254}$* precoated plastic plates. Column chromatography (CC): silica gel *60* (70–230 mesh) from *Merck* (Darmstadt). HPLC: system from *Shimadzu* (Duisburg, Germany), *Gilson 305* pumps, *Shimadzu-SPD-M10AV* UV/VIS detector; 0.8 ml/min for anal. and 8 ml/min for prep. separations; injection volume (prep.) 500 µl (100 mg of isomer mixture); UV detection (diode array) at 210 nm; capillary temp. kept at r.t. GC: *Hewlett-Packard-6890* system; H_2 as mobile phase; flow rate 1.7 ml min^{-1}; flame-ionization detection (FID) at 330°; injector temp. 240° and injection volume 0.1 µl as the temp. was rised from 60° to 300° at the ramp rate 8° min^{-1} for the optimized chromatogram. All chromatograms were processed by ColaChrom software (Version 8.1) developed by MPI für Kohlenforschung, Mülheim, Germany. IR Spectra: *Nicolet-320-FT-IR* and *Bruker-Tensor-27* spectrometer; KBr pellets or thin films, $\tilde{\nu}$ in cm^{-1}, ^{1}H- and ^{13}C-NMR Spectra: *Bruker-DRX-400* spectrometer at 400.1 (^{1}H) and 100.6 MHz (^{13}C); chemical shifts δ in ppm with $SiMe_4$ or residual nondeuterated solvent as internal standard ($CDCl_3$: δ(H) 7.26, δ(C) 77.00), coupling constants J in Hz. Mass spectra: *Finnigan-MAT-8430* spectrometer, electron ionization (EI) at 70 eV, in *m*/*z* (rel. %); GC/MS: *Carlo-Erba-HRGC-5160* gas chromatograph (*DB* 1–0.25 µm-fused-silica capillary column; 30 m × 0.31 mm i.d.; carrier gas Ar) attached to a *Finnigan-MAT-4515* spectrometer (EI at 40 eV).

*2,3-Dihydro-2-octyl-1*H*-inden-1-one* (**4**). A mixture of 1-phenyldecan-1-one (**2**; 25 g, 0.107 mol), hexamethylenetetramine (36 g, 0.26 mol), and Ac_2O (34 g, 0.33 mol) was heated at 80° for 4 h under N_2. The mixture was cooled to 30° and poured into a stirred mixture of CH_2Cl_2 (150 ml) and 2N NaOH (150 ml). The org. layer was washed with 1N aq. HCl (80 ml) and then azeotropically dried and concentrated to 50 ml by distilling the CH_2Cl_2. The soln. containing 2-methylene-1-phenyldecan-1-one (**3**) was used without further purification in the next step. It was added to conc. H_2SO_4 soln. (110 ml) at a rate such that the temp. was maintained between 50–60°, while the CH_2Cl_2 was removed by distillation and N_2 flushed in. The mixture was stirred at 50–60° for 1 h, cooled to 20° and quenched with a stirred mixture of CH_2Cl_2 (150 ml) and H_2O (150 ml). After separating the aq. layer, the org. layer was concentrated, dried ($MgSO_4$) and filtered through silica gel: 18 g (69%) of **4**. Light yellow oil. R_f (SiO_2, pentane/CH_2Cl_2 6:4) 0.4. B.p. 140°/5 Torr. IR (film): 1710*s*, (C=O); 2933, 2960*s* (CH, stretch.), 3073, 3033*w* (CH, stretch., arom.), 1610*m* (C=C, arom.). ^{1}H-NMR (400.1 MHz, $CDCl_3$): 0.80 (*t*, ^3J = 6.88, *Me*$(CH_2)_7$); 1.16–1.93 (*m*, Me(C*H*$_2)_7$); 2.55–2.76 (*m*, $CH_2(3)$), 3.11–3.27 (*m*, H–C(2)); 7.26–7.30 (*m*, H–C(6)); 7.36–7.38 (*d*, ^3J = 7.7, H–C(4)); 7.48–7.51 (*m*, H–C(5)); 7.66–7.68 (*d*, ^3J = 7.8, H–C(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 209.08 (*s*, C(1)); 32.86 (*t*, C(3)); 47.48 (*d*, C(2)); 123.83 (*d*, C(6)); 127.26 (*d*, C(4)); 126.51 (*d*, C(5)); 134.56 (*d*, C(7)); 153.77 (*s*, C(7a)); 136.85 (*s*, C(3a)); 14.07 (*q*, *Me*$(CH_2)_7$); 22.63 (*t*, Me*C*

$H_2(CH_2)_6$); 31.83 (*t*, $MeCH_2CH_2(CH_2)_5$); 31.46 (*t*, $Me(CH_2)_6CH_2$); 29.24 (*t*); 29.44 (*t*), 29.61 (*t*). EI-MS (70 eV): 244 (2, M^+), 145 (5, $[M^+ - C_7H_{15}]^+$), 132 (100, $[M^+ - C_8H_{16}]^+$), 131 (4, $[M - C_8H_{17}]^+$), 115 (3, $[131 - O]^+$), 103 (3, $[131 - CO]^+$).

*2′,3′-Dihydrospiro[1,3-dithiolane-2,1′-[1*H*]indene]* (**5**). A soln. of **4** (18 g, 0.0737 mol) in $BF_3 \cdot Et_2O$ (30 g, 27.25 ml, 0.217 mol) was treated with ethane-1,2-dithiol (10.02 g, 0.106 mol), and the mixture was stirred at r.t. for 6 h. The mixture was diluted with MeOH (60 ml) and the org. layer separated. The solvent was evaporated and the residue purified by CC (silica gel, pentane, pentane/CH_2Cl_2 2 : 1): 18.9 g (80%) of **5**. Colorless liquid. R_f (SiO_2, pentane/CH_2Cl_2 6 : 3) 0.7. B.p. 230°/5 Torr. IR (film): 3022*m* (CH, stretch., arom.), 2956, 2925, 2869*s* (CH, stretch., aliph.), 1603*m* (C=C, conj.). ^{1}H-NMR (400.1 MHz, $CDCl_3$): 0.81 (*t*, $^3J = 6.8$, *Me*$(CH_2)_7$); 1.18–1.84 (*m*, Me(C*H*$_2)_7$); 2.43–2.45 (*m*,$CH_2(3')$); 2.88–2.93 (*m*, H–C(2′)); 3.27–3.46 (*m*, $CH_2(4)$, $CH_2(5)$); 7.04–7.16 (*m*, 4 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 14.10 (*q*, *Me*$(CH_2)_7$); 22.66 (*t*, Me*C*$H_2(CH_2)_6$); 28.23 (*t*); 29.96 (*t*); 31.86 (*t*); 36.57 (*t*); 29.31 (*t*, C(3′)); 29.37 (*t*, $MeCH_2CH_2(CH_2)_5$); 40.94, 40.48 (2*t*, $CH_2(4)$, $CH_2(5)$); 54.63 (*d*, C(2′)); 124.31, 124.20 (2*d*, C(5′), C(6′)); 127.08, 127.70 (2*d*, C(4′) C(7′)); 140.67 (*s*, C(1′)); 148.40 (*s*, C(3′a), C(7′a)). GC/MS): 320 (40, M^+), 292 (78, $[M - C_2H_4]^+$), 259.2 (80, $[M - C_2H_5S]^+$), 227.2 (10, $[M - C_2H_5S_2]^+$), 180 (98, $[292.1 - C_8H_{16}]^+$), 179 (100, $[292.1 - C_8H_{17}]^+$), 148.1 (60, $[180 - S]^+$).

*2,3-Dihydro-2-octyl-1*H*-indene* (**7**). A mixture of **5** (18 g, 0.056 mol) and *Raney* Ni (100 g) in 95% EtOH (300 ml) was refluxed for 8 h. The cooled mixture was filtered, the filtrate diluted with H_2O (100 ml) and extracted with Et_2O (2 × 100 ml), and the combined Et_2O extract washed with H_2O, dried (Na_2SO_4), concentrated, and purified by passing through a small column of silica gel: 7 g (78%) of **7**. Colorless liquid. R_f (SiO_2, pentane) 0.6: B.p. 140°/14 Torr. IR (film): 2956*s* (CH, stretch., aliph.), 2928*s* (CH, stretch., aliph.), 3043, 3022*m* (CH, stretch., arom.), 1378*m* (CH_3, def.), 1601*s* (C=C arom.). ^{1}H-NMR (400.1 MHz, $CDCl_3$): 0.97 (*t*, $^3J = 6.7$, *Me*$(CH_2)_7$); 1.33–2.52 (*m*, Me(C*H*$_2)_7$, H–C(2)); 2.61–3.13 (*m*,$CH_2(1)$, $CH_2(3)$); 7.17–7.26 (*m*, 4 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 14.11 (*q*, *Me*$(CH_2)_7$); 22.69 (*t*, Me*C*$H_2(CH_2)_6$); 31.92 (*t*, $MeCH_2CH_2$-$(CH_2)_5$); 35.83 (*t*, $Me(CH_2)_6CH_2$); 29.85 (*t*); 29.66 (*t*); 29.35 (*t*); 28.44 (*t*); 39.37 (2 *t*, C(1) C(3)); 40.27 (*d*, C(2)); 124.34 (2*d*, C(5) C(6)); 125.94 (2*d*, C(4) C(7)); 143.70 (2*s*, C(3a) C(7a)). EI-MS (70 eV): 230 (50, M^+), 131 (30, $[M - C_7H_{15}]^+$), 117 (100, $[M - C_8H_{17}]^+$), 104 (40, $[117 - CH]^+$). HR-MS: 232.2185 + 2 ppm ($C_{17}H_{26}^+$; calc. 232.2191).

*2,3,4,7-Tetrahydro-2-octyl-1*H*-indene* (**8**). A mixture of **7** (14.5 g, 62.5 mmol), liq. NH_3 (87 ml), EtOH (100 ml), and THF (60 ml, dry) was cooled to −75° (MeOH/liq. N_2 bath). Sodium metal was added under mechanical stirring until the blue color persisted for 20 min. The NH_3 was allowed to evaporate overnight. The remaining residue was partitioned between Et_2O and H_2O. The Et_2O layer was evaporated and the resulting liquid again partitioned between Et_2O and H_2O. The Et_2O layer was dried ($MgSO_4$) and evaporated: crude **8** (13.55 g, 93%). Colorless liquid. The product was rather unstable and on standing slowly re-oxidized to **7**, it was thus quickly used for further reaction **8**. R_f (SiO_2, pentane) 0.7. B.p. 140°/7 Torr. IR (film): 3026*m* (C–H, stretch.), 2956, 2915, 2874*s* (CH, stretch.), 1377*m* (CH_3, def.). ^{1}H-NMR (400.1 MHz, $CDCl_3$): 0.93 (*t*, $^3J = 6.8$, *Me*$(CH_2)_7$); 1.28–1.64 (*m*, Me(C*H*$_2)_7$, H–C(2)); 1.95–2.30 (*m*, $CH_2(1)$, $CH_2(3)$); 2.66 (br. *s*, $CH_2(4)$, $CH_2(7)$); 5.79 (br. *s*, H–C(5), H–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 14.12 (*q*, *Me*$(CH_2)_7$); 22.71 (*t*, Me*C*$H_2(CH_2)_6$); 27.56 (2*t*, C(4), C(7)); 28.40 (*t*); 29.38 (*t*); 29.70 (*t*); 29.90 (*t*); 31.29 (*t*); 36.24 (*d*, C); 37.06 (*t*, $MeCH_2CH_2/CH_2)_5$); 42.22 (2*t*, C(1), C(3)); 124.77 (2*d*, C(5), C(6)); 130.97 (*s*, C(3a), (7a)). GC/MS: 232.2 (47, M^+), 133.2 (5, $[M - C_7H_{15}]^+$), 119.1 (100, $[M - C_8H_{17}]^+$), 92.1 (80, $[119.1 - C_2H_3]^+$).

Ethyl rel-*(1a*R*,4*S*,6a*S*) and* rel-*(1a*R*,4*R*,6a,*S*)-1,1a,2,3,4,5,6,6a-Octahydro-4-octylcyclopropa[*f*]indene-1-carboxylate* (**9a** and **9b**, resp.), *and Ethyl 2,3,4,7-Tetrahydro-2-octyl-1*H*-3a,7a-methanoindene-8-carboxylate* (**10**). To a refluxing suspension of **8** (14.5 g, 62.50 mmol), anh. $CuSO_4$ (7.5 g) and anh. cyclohexane (70 ml) was added dropwise with stirring within 5 h, a soln. of ethyl diazoacetate (34.69 g, 304.0 mmol) in anh. cyclohexane (150 ml). The mixture was refluxed for further 60 min and filtered to remove the $CuSO_4$. The soln. was evaporated and the product separated by CC (silica gel, pentane → pentane/CH_2Cl_2 of increasing polarity). Some unreacted **8** eluted first, followed by **9a**/**9b**/**10**/**11** (12 g, 56%), and finally by diethyl fumarate (by-product). The mixture **9a**/**9b**/**10**/**11** was further separated by reversed-phase HPLC as described in the *General Part*: **9a**, **9b**, and **10**.

Data of **9a**: Colorless solid. R_f (SiO_2, pentane/CH_2Cl_2 3 : 1) 0.52. M.p. 37–39°. IR (film): 2956*m* (CH, stretch.), 1724*s* (C=O), 1376*m* (CH_3, def.), 1213, 1172*s*, (C–O). ^{1}H- and ^{13}C-NMR: *Table.* GC/MS: 318 (26, M^+), 289 (5, $[M - C_2H_5]^+$), 245 (10, $[M - C_3H_5O_2]^+$), 205 (15, $[M - C_8H_{17}]^+$), 131 (27, $[205 - C_3H_6O_2]^+$), 112 (100, $C_8H_{16}^+$). HR-MS: 341.24465 + 1.30 ppm ($C_{21}H_{34}NaO_2^+$, $[M + Na]^+$; calc. 341.245649).

Data of **9b**: Colorless solid. R_f (SiO_2, pentane/CH_2Cl_2 3:1) 0.42. M.p. 47–49°. IR (film): 2956*m* (CH, stretch.), 1724*s* (C=O), 1376*m* (CH_3, def.), 1213, 1172*s* (C–O). ^{1}H- and ^{13}C-NMR: *Table.* GC/MS: 318 (28, M^+), 289 (5, $[M-C_2H_5]^+$), 245 (10, $[M-C_3H_5O_2]^+$), 205 (18, $[M-C_8H_{17}]^+$), 131 (36, $[205-C_3H_6O_2]^+$), 112 (100, $C_8H_{16}^+$). HR-MS 341.244629 + 1.39 ppm ($C_{21}H_{34}NaO_2^+$, $[M+Na]^+$: calc. 341.245649).

Data of **10**: Colorless liquid. R_f (SiO_2, pentane/CH_2Cl_2 3:1) 0.61. IR. (film): 2956*m* (CH, stretch.), 1724*s* (C=O), 1376*m* (CH_3, def.), 1213, 1172*s* (C–O). ^{1}H- and ^{13}C-NMR: *Table.* MS/GC: 318 (5, M^+), 273 (21, $[M-CO_2H]^+$), 245 (20, $[M-CO_2Et]^+$), 230 (100, $[245-CH_3]^+$), 205 (25, $[M-C_8H_{17}]^+$), 131 (73, $[205-C_3H_6O_2]^+$), 117 (50, $[131-CH_2]^+$), 91 (45, $[117-C_2H_4]^+$). HR-MS: 341.244790 + 0.92 ppm ($C_{21}H_{34}NaO_2^+$, $[M+Na]^+$; calc. 341.245649).

rel-*(1a*R*,4*S*,6a*S*)- and* rel-*(1a*R*,4*R*,6a*S*)-1,1a,2,3,4,5,6,6a-Octahydro-4-octylcyclopropa[f]indene-1-carboxylic Acid* **12** and **13**, resp.). A mixture of EtOH (100 ml) and 1M NaOH (60 ml) was stirred for a while, and then **9a** (0.5 g, 1.46 mmol) was added slowly. The mixture was kept at r.t. and stirred for 4–6 h (TLC monitoring). Then the mixture was acidified with 1M HCl. The EtOH was evaporated and the residual aq. phase extracted with AcOEt (2×) and H_2Cl_2 (1×). The combined org. extract was washed with H_2O, dried ($MgSO_4$), and evaporated and the residue purified by CC (silica gel, CH_2Cl_2 (→ impurities) then Et_2O): 0.3 g (71%) of **12**. Colorless solid which was recrystallized from hexane/CH_2Cl_2. As described for **12**, **13** was prepared from **9b** in 75% yield.

Data of **12**: R_f (SiO_2, AcOEt/CH_2Cl_2 1:5) 0.49. M.p. 90–93°. IR (film): 2956*m* (CH, stretch.), 1724*s* (C=O), 1376*m* (CH_3, def.), 1213, 1172*s* (C–O). ^{1}H-NMR (400.1 MHz, $CDCl_3$): 0.89 (*t*, ^3J = 6.8, *Me*(CH_2)$_7$); 1.26 (br. *s*, Me(C*H*$_2$)$_7$); 1.44 (*t*, ^3J = 4.2, H–C(1)); 1.82 (br. *s*, H–C(1a), H–C(6a)); 1.32 (*m*,H–C(4)), 2.31 (br. *s*, CH_2(2), CH_2(6)); 1.87 (*dd*, *J* = 5.8, 13.2, H_β–C(3), H_β–C(5)); 2.25 (*dd*, *J* = 8.3, 13.2, H_α–C(3), H_α–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 14.02 (*q*, *Me*(CH_2)$_7$); 22.69 (*d*, C(1)); 23.27 (*t*, Me*C*H$_2$(CH_2)$_6$), 23.37 (2*t*, C(2), C(6)); 24.20 (2*d*, C(1a), (6a)), 28.28 (*t*, Me(CH_2)$_5$*C*H$_2$*C*H$_2$), 29.34, 29.72, 29.89 (3*t*, Me(CH_2)$_2$(*C*H$_2$)$_3$(CH_2)$_2$); 31.85 (*t*, MeCH$_2$*C*H$_2$(CH_2)$_5$); 36.21 (*d*, C(4)); 36.87 (*t*, Me(CH_2)$_6$*C*H$_2$); 42.47 (2*t*, C(3), C(5)); 128.84 (2*s*, C(2a), C(5a)); 181.06 (*s*, C=O). EI-MS: 290 (100, M^+), 177 (70, $[M-C_8H_{17}]^+$), 207 (10, $[M-C_6H_{11}]^+$), 131 (40, $[177-HCO_2H]^+$), 105 (30, $[131-C_2H_4]^+$). HR-MS 290.224146 + 1.50 ppm ($C_{19}H_{30}O_2^+$; calc. 290.224580).

Data of **13**: R_f (SiO_2, AcOEt/CH_2Cl_2 1:5) 0.45. M.p. 94–96°. IR (film): 2956*m* (CH, stretch.), 1724*s* (C=O), 1376*m* (CH_3, def.), 1213, 1172*s* (C–O). ^{1}H-NMR (400.1 MHz, $CDCl_3$): 0.86 (*t*, ^3J = 6.8, *Me*(CH_2)$_7$); 1.24 (br. *s*, Me(C*H*$_2$)$_7$); 1.38 (*t*, ^3J = 4.2, H–C(1)); 1.80 (br. *s*, H–C(1a), H–C(6a)); 2.10 (*m*, H–C(4)); 2.30 (br. *s*, CH_2(2), CH_2(6)); 1.75 (*dd*, *J* = 5.8, 15.1,H_β–C(3), H_β–C(5)); 2.35 (*dd*, *J* = 6.6, 15.1,H_α–C(3), H_α–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 14.51 (*q*, *Me*(CH_2)$_7$); 22.69 (*t*, Me*C*H(CH_2)$_6$); 23.29 (*d*, C(1)); 23.37 (2*d*, C(1a), C(6a)); 24.15 (2*t*, C(2), C(6)); 28.21 (*t*, Me(CH_2)$_5$*C*H$_2$*C*H$_2$), 29.34, 29.66, 29.84 (3*t*, Me(CH_2)$_2$(*C*H$_2$)$_3$(CH_2)$_2$); 31.87 (*t*, MeCH$_2$*C*H$_2$-(CH_2)$_5$), 35.66 (*d*, C(4)); 37.05 (*t*, Me(CH_2)$_6$*C*H$_2$); 42.53 (2*t*, C(3), C(5)); 129.00 (2*s*, C(2a), C(5a)); 180.75 (*s*, C=O). EI-MS: 290 (100, M^+), 207 (12, $[M-C_6H_{11}]^+$), 177 (75, $[M-C_8H_{17}]^+$), 131 (45, $[177-HCO_2H]^+$), 105 (25, $[131-C_2H_4]^+$). HR-MS: 290.224421 + 0.55 ppm ($C_{19}H_{30}O_2^+$; calc. 290.224580).

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