EPR Studies on Carboxylic Esters, 22 [1, 2]. Preparation of New Alkyl Azulenecarboxylates and EPR-spectroscopic Study of Their Radical Anions

Jürgen Voss[a], Thomas Pesel[a], Dirk Buddensiek[a], and Juuso Lehtivarjo[b]

[a] Fachbereich Chemie – Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

[b] School of Pharmacy, University of Eastern Finland, P. O. Box 1627, FI-70211 Kuopio, Finland

Reprint requests to Prof. Dr. Jürgen Voss. Fax: +49 (0) 40 42838 5592.
E-mail: voss@chemie.uni-hamburg.de

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Five regio-isomeric alkyl azulenecarboxylates were prepared. Additional substituents such as *tert*-butyl groups or deuterium were introduced in certain positions of the azulene skeleton in order to facilitate the assignment of the proton hyperfine structure (hfs) coupling constants of the EPR spectra. The electrochemical behavior of the esters was studied by means of differential pulse polarography and cyclovoltammetry. *In-situ* electroreduction of the azulenecarboxylic esters led to the corresponding radical anions, the EPR spectra of which were recorded. The spin density distribution in these non-alternant systems as determined from hfs coupling constants was compared with the results of MO calculations and discussed with respect to the influence of substituents.

Key words: Alkyl Azulenecarboxylates, Polarography, Cyclovoltammetry, EPR Spectroscopy, Quantum Chemical Calculations

Introduction

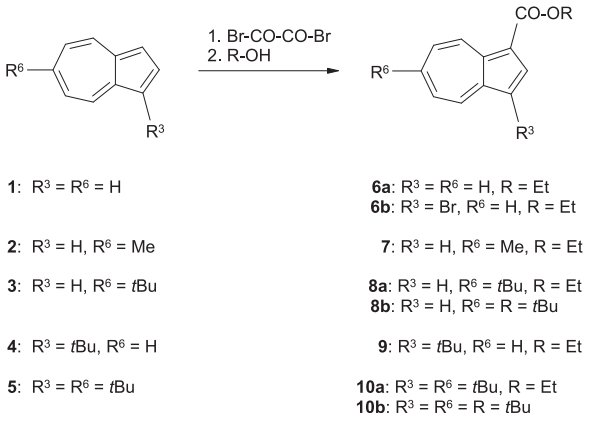
In the past, we have studied the EPR spectra of alkyl naphthalenecarboxylate [3], *O*-alkyl naphthalenecarbothioate and alkyl naphthalenecarbodithioate [4] radical anions. Our investigations were aimed at the determination of the spin density distribution in condensed arenes and the changes which would occur after an electronic disturbance by substitution with electron-withdrawing ester groups in certain positions. Naphthalene belongs to the category of alternating π-electron systems. Azulene, on the other hand, represents its non-alternating counterpart. Radical ions of this type of compounds exhibit quite different spin density distributions as compared with the alternating isomers. Within the framework of the HMO theory, the pairing theorem predicts an identical spin distribution in the radical cation and the corresponding radical anion of a species with alternating π electrons. This is, however, not valid for non-alternating systems [5 – 8] as clearly demonstrated experimentally by Gerson's group for the EPR spectra of azulene and alkylazulene radical anions [9] and radical cations [10].

Functional derivatives of azulene have not yet been investigated by EPR spectroscopy. We therefore present here the results of our studies on the carboxylic esters of azulene, *i. e.* of derivatives with electron-withdrawing substituents, which were to compare with the related naphthalene derivatives.

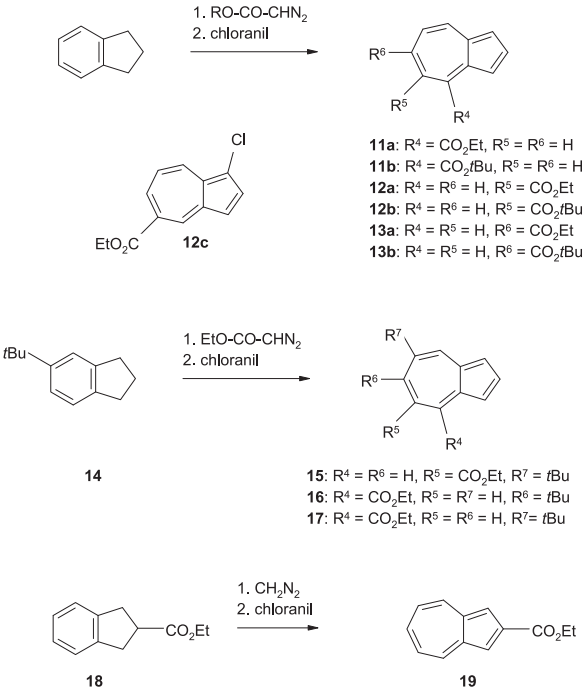
Results and Discussion

Preparations

In view of our aim to determine the proton hyperfine structure (hfs) coupling constants and, in particular, to assign these to the specific positions in the azulene system, we were interested in preparing *tert*-butyl azulenecarboxylates possibly with additional *tert*-butyl substituents in the ring, besides the corresponding ethyl esters. This was important because the low symmetry of azulene as compared



Scheme 1. Preparation of alkyl azulene-1-carboxylates by carbobromination.



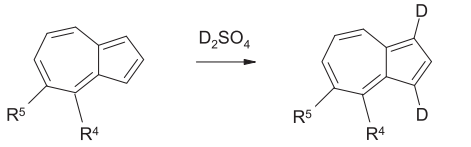
Scheme 2. Preparation of alkyl azulenecarboxylates by ring enlargement.

with its isomer naphthalene would cause EPR spectra with large numbers of lines, which can be reduced by replacement of protons with *tert*-butyl groups or deuterons. Furthermore, these substituents can serve as labels for the assignments. In addition to azulene (**1**) [11] and 6-methylazulene (**2**) [12], we have therefore prepared 6-*tert*-butylazulene (**3**) [13] by Ziegler-Hafner-type syntheses from pyridine, 4-picoline and 4-*tert*-butylpyridine, respectively. The desired 4-*tert*-butylazulene could not be prepared from 2-*tert*-butylpyridine [14] because the latter was totally unreactive towards the Ziegler-Hafner reagent 2,4-dinitrochlorobenzene. Also, an attempted nucleophilic *tert*-butylation of **1** with *tert*-butyllithium did not lead to 4-*tert*-butylazulene. Instead, the less sterically hindered isomer **3** was formed as the only product with 78 % yield in contrast to the literature [15], and 4,6′-biazulenyl [16] instead of 4-*tert*-butylazulene or **3** was formed by the reaction of **1** with *tert*-butylmagnesium chloride. Thus, 4-*tert*-butylazulene still remains an unknown compound! 1-*tert*-Butylazulene (**4**) was obtained by Friedel-Crafts *tert*-butylation of **1** [13]. Furthermore, electrophilic *tert*-butylation of indane gave 5-*tert*-butylindane (**14**) [17] which represents another suitable starting compound for *tert*-butylazulene derivatives by carbene insertion reactions.

Mainly two different methods were applied for the preparation of the desired alkyl azulenecarboxylates: Carbobromination of an azulene with subsequent alcoholysis (Scheme 1), and ring enlargement (carbene insertion) of an indole with alkyl diazoacetate (Scheme 2).

We preferred to use the regioselective carbobromination method of W. Treibs [18] rather than the related dangerous and inconvenient phosgenation reaction described by the same author [19]. The intermediate acid bromides were not isolated but directly reacted with alcohols in a one-pot reaction. In this way we obtained ethyl azulene-1-carboxylate (**6a**) from azulene (**1**). A small amount of ethyl 3-bromoazulene-1-carboxylate (**6b**) was formed as by-product. Starting with 6-methylazulene (**2**) or 6-*tert*-butylazulene (**3**) led to the corresponding esters **7**, **8a** and **8b**, respectively (Scheme 1). Carbobromination of **4** and of 1,6-di-*tert*-butylazulene (**5**), prepared by Friedel-Crafts *tert*-butylation of **3**, gave the corresponding acid bromides. Subsequent alcoholysis yielded the esters **9**, **10a** and **10b** (Scheme 1).

Further alkyl azulenecarboxylates were prepared from indanes by ring enlargement with alkyl diazoacetates. This method has also been described by W. Treibs [20]. The reaction of unsubstituted indane with ethyl diazoacetate and subsequent dehydrogenation with chloranil led to a mix-



11a: $R^4 = CO_2Et$, $R^5 = H$ **11c**: $R^4 = CO_2Et$, $R^5 = H$
12a: $R^4 = H$, $R^5 = CO_2Et$ **12f**: $R^4 = H$, $R^5 = CO_2Et$
12d: $R^4 = H$, $R^5 = CO_2Me$ **12e**: $R^4 = H$, $R^5 = CO_2Me$

Scheme 3. Deuteration of alkyl azulene-4- and azulene-5-carboxylate.

ture of three isomeric ethyl azulenecarboxylates **11a** (1.5%), **12a**, (6.9%) and **13a** (2.3%) together with ethyl 1-chloroazulene-5-carboxylate **12c** as by-product. If *tert*-butyl diazoacetate was used as reagent the corresponding three *tert*-butyl esters **11b** (1.3%), **12b** (2.5%) and **13b** (0.5%) were formed (Scheme 2).

Ring enlargement of 5-*tert*-butylindane (**14**) with ethyl diazoacetate was also achieved. It resulted in a mixture of the three ethyl esters **15** (2.8%), **16** (9.4%) and **17** (10.7%). Obviously, **15** had been formed by insertion of the ethoxycarbonylcarbene between C-6 and C-7 of **14**, whereas **16** originated from the insertion between C-3a and C-4, and **17** by insertion between C-7 and C-7a of the indane **14** (Scheme 2). Although ethyl indane-2-carboxylate (**18**) is less reactive, its reaction with diazomethane at least led to 1.4% ethyl azulene-2-carboxylate (**19**). Only recently, the preparation of **19** with a higher yield of 50% by Pd(0)-catalyzed coupling reaction of azulene-2-boronic acid with ethyl chloroformate was described, and the authors state **19** to be "difficult to access by conventional methods" [21].

Although the yields are low, this method represents a good choice for the synthesis since simple starting compounds are used and only one step is necessary. Even the lack of regioselectivity is fortunate as each three of the desired esters are obtained on one strike, which can be separated by column or, as in the tricky case of **12c**/**13a**, by preparative gas/liquid chromatography. The esters were identified and their structures determined by NMR spectroscopy.

In certain special cases, other synthetic methods were applied. Direct regioselective, acid-catalyzed deuteration in the five-membered ring of **11a**, **12a** and **12d** gave the corresponding 1,3-dideutero derivatives **11c**, **12f** and **12e** (Scheme 3).

Table 1. Polarographic reduction potentials E_{red} (V) and cyclovoltammetric peak current ratios i_{pa}/i_{pc} of alkyl azulenecarboxylates.

Compound	$E_{red}(1)$	$E_{red}(2)$	$E_{red}(3)$	$i_{pa}/i_{pc}(1)$
6a	−0.73	−1.70		0.45
6b	−0.55	–		0.38
7	−0.85	−1.85		0.61
8a	−0.89	−1.82		1.00
8b	−0.88	−1.88		1.00
9	−0.80	−1.48		0.84
10a	−0.95	−1.95		0.77
10b	−0.95	−1.90		1.00
19	−0.68	−1.54		0.62
11a	−0.54	−1.25		0.93
16	−0.89	−1.54		1.00
12a	−0.79	−1.78		0.70
12b	−0.85	−1.82		0.52
15	−0.86	−1.78		1.29
13a	−0.69	−1.40		1.00

Electroanalytical results

In order to find out the reduction potentials and to get information on the reversibility of the electron transfer processes, electroanalytical measurements were performed. The reduction (peak) potentials E_{red} of the esters **6**–**19** are compiled in Table 1. They were measured by the use of the differential pulse polarographic (DPP) method with an internal Ag wire as reference electrode [22]. The peak with the lowest cathodic reduction potential $E_{red}(1)$ can be assigned to the single electron transfer (SET) step which leads to the formation of a radical anion. It represents thus the deciding step in view of the EPR measurements. Another reduction peak $E_{red}(2)$ is observed at a more negative reduction potential (see Table 1) which can be assigned to the formation of a diamagnetic dianion.

Inspection of the reduction potentials E_{red} in Table 1 reveals that the various ethyl azulenecarboxylates do not exhibit particularly noticeable differences. Only ethyl azulene-4-carboxylate (**11a**) seems to be reduced at a significantly lower reduction potential compared with the other regioisomers. The observed substituent effects are as expected. The electron withdrawing bromo substituent in **6b** causes a shift in the positive direction whereas due to their +I-effect methyl and, more pronounced, *tert*-butyl groups shift $E_{red}(1)$ to more negative values; compare *e. g.* **6a** with **7**, **8a**, **9**, and **10a**.

Cyclovoltammetric measurements revealed that the radical anions formed at the first SET step in most

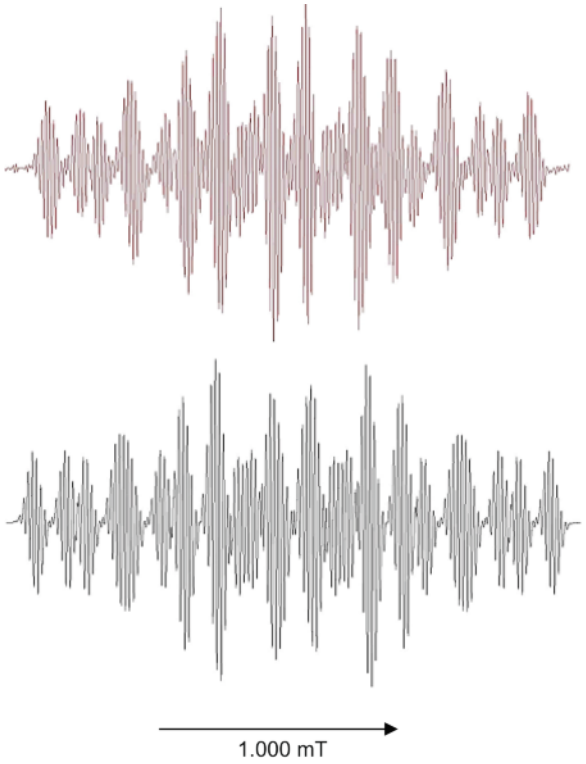


Fig. 1. Experimental (top) and simulated (bottom) EPR spectrum of the ethyl 6-*tert*-butylazulene-1-carboxylate radical anion (**8a**$^{\bullet-}$).

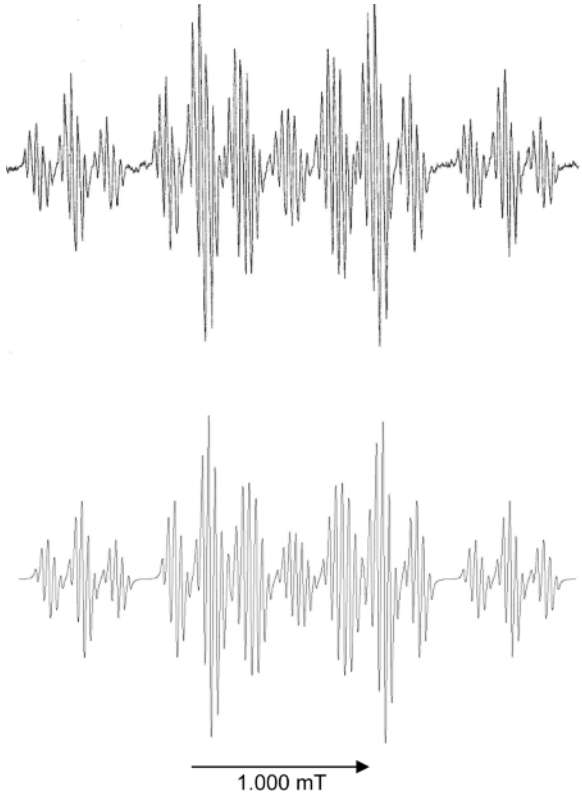


Fig. 2. Experimental (top) and simulated (bottom) EPR spectrum of the ethyl azulene-2-carboxylate radical anion (**19**$^{\bullet-}$).

cases should be persistent enough as to allow EPR spectra to be recorded successfully after *in situ* electroreduction, since peak current ratios of $i_{pa}/i_{pc}(1) > 0.4$ were observed (see Table 1). The radical anion of **6b** [$i_{pa}/i_{pc}(1) = 0.38$] readily eliminates a bromide ion. Therefore, it cannot be detected by EPR spectroscopy and a reduction wave due to the formation of a dianion is missing.

Electron paramagnetic resonance results

Radical anions of the esters were generated by internal electroreduction at appropriate potentials and temperatures in a flat quartz cell within the cavity of the EPR spectrometer [23, 24]. In most cases the recorded spectra exhibit large numbers of lines (see Figs. 1 – 3) since the symmetry of the azulene derivatives is low. Nevertheless, valid sets of proton hyperfine structure (hfs) coupling constants a^H could be determined (see Table 2) by simulation of the spectra.

The assignment of the proton coupling constants to particular positions was, on the other hand, not straightforward in many cases. It was achieved by comparison of species substituted with deuterium or *tert*-butyl groups, and with values calculated from MO spin densities by use of the McConnell equation $a_\mu^H = Q\,\rho_\mu^\pi$.

We could not record an EPR spectrum of the unsubsituted ethyl azulene-1-carboxylate radical anion **6a**$^{\bullet-}$. Even at low temperature the radical anion was not persistent enough. Although we observed an EPR spectrum after *in situ* electroreduction of ethyl 6-methylazulene-1-carboxylate (**7**), we were not able to analyze it because of its low signal-to-noise ratio and its irregular and asymmetric shape. Therefore, a valid assignment of this spectrum to the expected radical anion **7**$^{\bullet-}$ was not possible. The 6-*tert*-butyl derivative **8a**$^{\bullet-}$, on the other hand, yielded a well resolved multi-line EPR spectrum (Fig. 1) at 18 °C which was reproduced by simulation with the six coupling constants given in Table 2. Comparison with the spectrum

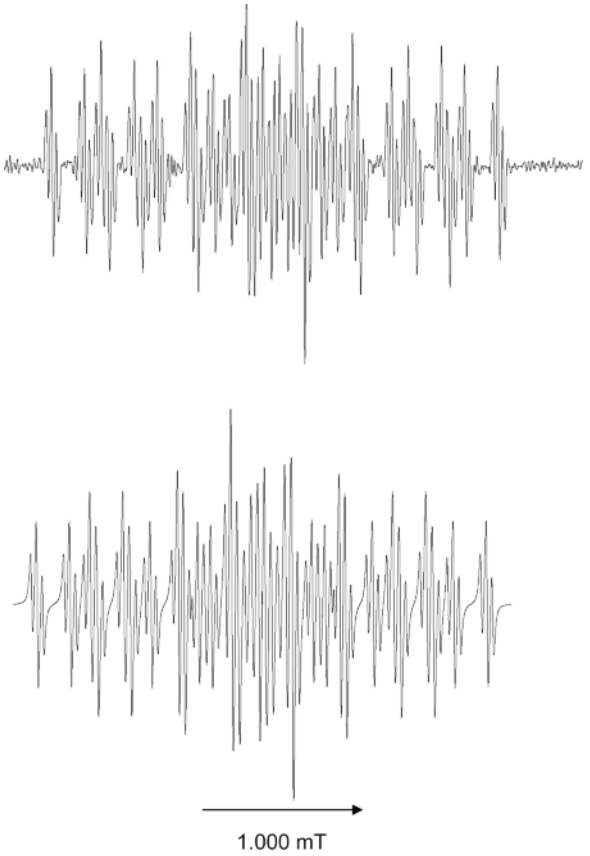


Fig. 3. Experimental (top) and simulated (bottom) EPR spectrum of the ethyl azulene-5-carboxylate radical anion (**12a**$^{\bullet-}$).

of the ethyl 3-*tert*-butylazulene-1-carboxylate radical anion 9$^{\bullet-}$ provided the large coupling constant $a_6^{\mathrm{H}} = 0.907$ mT which also gave rise to the very large total width of the spectrum ($\Delta H = 2.90$ mT). The EPR spectra of the ethyl 3,6-di-*tert*-butyl- (**10a**$^{\bullet-}$), *tert*-butyl 6-*tert*-butyl- (**8b**$^{\bullet-}$) and *tert*-butyl 3,6-di-*tert*-butylazulene-1-carboxylate (**10b**$^{\bullet-}$) radical anions allowed the assignment of several further experimental coupling constants a_μ^{H} (see Table 2). They are in reasonable agreement with the a_μ^{H} value obtained by MO calculations.

Ethyl azulene-2-carboxylate radical anions (**19**$^{\bullet-}$) gave a well resolved EPR spectrum (Fig. 2), which was easier to analyze because of the higher symmetry of **19** compared with **8a**. The five coupling constants a_μ^{H} given in Table 2 were assigned by considering the multiplicity of the lines (*e. g.* the large splitting of 0.870 mT for H-6) and by MO calculations.

The radical anions of ethyl azulene-4-carboxylate (**11a**$^{\bullet-}$) once more gave an EPR spectrum which was difficult to analyze. Finally, the seven different coupling constants a_μ^{H} of **11a**$^{\bullet-}$ could be determined and assigned with the help of a comparison with its 6-*tert*-butyl (**16**$^{\bullet-}$), 7-*tert*-butyl (**17**$^{\bullet-}$) and 1,3-dideutero (**11c**$^{\bullet-}$) derivatives, and with the *tert*-butylester **11b**$^{\bullet-}$ (see Table 2).

The *in situ* electroreduction of ethyl azulene-5-carboxylate led to a well resolved EPR spectrum of the corresponding radical anion **12a**$^{\bullet-}$ (Fig. 3). The assignment of the coupling constants was possible by comparison with the 1,3-dideutero derivative **12f**$^{\bullet-}$ and the 7-*tert*-butyl derivative **15**$^{\bullet-}$ (see Table 2). The EPR spectrum of the *tert*-butyl azulene-5-carboxylate radical anion **12b**$^{\bullet-}$ exhibited a low signal-to-noise ratio and was overlapped with a more intense spectrum of unknown origin. Methyl 1,3-dideuteroazulene-5-carboxylate (**12e**) led to an asymmetric multi-line spectrum which we could not interpret appropriately. Radical anions of the 1-chloro derivative **12c**$^{\bullet-}$ are not persistent because of rapid chloride elimination and concomitant decomposition of the resulting radical [25].

The higher symmetry of the radical anions of ethyl azulene-6-carboxylate (**13a**$^{\bullet-}$) facilitated the assignment of the coupling constants. Comparison with the spectrum of the *tert*-butyl ester **13b**$^{\bullet-}$ allowed the assignment of the 0.062 mT splitting observed in **13a**$^{\bullet-}$ to the OCH_2 protons which are missing in **13b**$^{\bullet-}$.

Inspection of Table 2 shows that splitting due to OCH_2 protons is only observed if the ethyl ester group occupies the 2-, 4- or 6-position of the azulene, *i. e.* the high spin density positions (see below).

Spin density distributions

Decades ago, Bernal, Rieger and Fraenkel have studied the EPR spectra of the radical anions of azulene (**1**$^{\bullet-}$) and several derivatives [26]. They have also performed McLachlan type MO calculations on the spin density distribution. The agreement between the theoretical spin densities ρ_μ^π and the values calculated from the experimentally observed proton hfs coupling constants a_μ^{H} by use of the McConnell relationship $\rho_\mu^\pi = a_\mu^{\mathrm{H}} Q^{-1}$ was rather moderate. The authors stated [26]: "McLachlan's... theory is... expected to be more accurate for alternant rather than non-alternant compounds. In the absence of elaborate

Table 2. EPR spectroscopic proton hfs coupling constants a_μ^H (mT) of alkyl azulenecarboxylate radical anions.

Radical anion	a_1^H	a_2^H	a_3^H	a_4^H	a_5^H	a_6^H	a_7^H	a_8^H	a_{OCH2}^H
1$^{\bullet-}$ [a]	0.027	0.395	0.027	0.622	0.134	0.883	0.134	0.622	–
8a$^{\bullet-}$	–	0.373	[b]	0.730	0.198	0.016[c]	0.126	0.590	[d]
8b$^{\bullet-}$	–	0.374	[b]	0.726	0.202	0.016[c]	0.149	0.587	–
9$^{\bullet-}$	–	0.375	[e]	0.726	0.174	0.907	0.133	0.586	[d]
10a$^{\bullet-}$	–	0.363	[e]	0.735	0.174	0.016[c]	0.136	0.590	[d]
10b$^{\bullet-}$	–	0.372	[e]	0.722	0.191	0.016[c]	0.143	0.552	–
19$^{\bullet-}$	0.033	–	0.033	0.637	0.170	0.870	0.170	0.637	0.028
11a$^{\bullet-}$	0.038	0.294	0.038	–	0.164	0.542	0.088	0.437	0.054
11b$^{\bullet-}$	0.038	0.284	0.038	–	0.162	0.542	0.088	0.437	–
11c$^{\bullet-}$	[f]	0.275	[f]	–	0.165	0.605	0.070	0.440	0.055
16$^{\bullet-}$	0.027	0.316	0.027	–	0.147	[e]	0.088	0.396	0.056
17$^{\bullet-}$	0.037	0.264	0.037	–	0.161	0.496	[e]	0.438	0.062
12a$^{\bullet-}$	0.029	0.197	0.029	0.353	–	0.824	0.310	0.945	[d]
12b$^{\bullet-}$	0.025	0.193	0.025	0.357	–	0.825	0.310	0.945	–
12f$^{\bullet-}$	[f]	0.210	[f]	0.350	–	0.820	0.290	0.950	[d]
15$^{\bullet-}$	[b]	0.320	[b]	0.320	–	0.830	[e]	0.960	[d]
13a$^{\bullet-}$	0.030	0.365	0.030	0.425	0.065	–	0.065	0.425	0.062
13b$^{\bullet-}$	0.023	0.365	0.023	0.425	0.065	–	0.065	0.425	–

[a] The proton hfs coupling constants of the azulene radical anion (**1**$^{\bullet-}$) were taken from ref. [26]; [b] $a_{1/3}^H$ was not observed; [c] splitting is due to the nine γ-protons of the *tert*-butyl substituent; [d] no splitting due to the *O*-CH_2 protons was observed; [e] no splitting due to the *tert*-butyl protons was detected; [f] no splitting due to the deuterons was detected.

calculations for the azulene anion and in spite of the shortcomings of the McLachlan theory we have been forced to resort to it in the following as the only simple procedure for obtaining an estimate of the ρ_i^π". Even the choice of a suitable π,σ spin polarization parameter Q turned out to be not possible since Q depends strongly on the bond angles in the skeleton of a π-electron system, and these vary within the azulene molecule and deviate significantly from the 120° value of regular sp^2 centers [26] in contrast to the situation in radical anions of alternating π-electron systems such as naphthalene [3]. In 1994, Gerson and coworkers investigated the radical anions of oligomethylazulenes and studied the influence of the methyl groups on the spin density distribution. They detected substituent effects when the even, high spin density positions 2, 4, 6 and 8 were methylated, whereas the effect of methyl groups in the odd, low spin density positions 1, 3, 5, and 7 was nearly negligible [9]. Interestingly, they relinquished any MO calculation in their study. In 1995, Waltman and Bargon [27] studied the 1-*tert*-butyl- and 1,3-di-*tert*-butylazulene radical anions by EPR spectroscopy. The proton hfs couplings were not significantly influenced by the *tert*-butyl substituents. Concerning the theoretical splitting constants as calculated at the INDO level by use of Hartree-Fock optimized geometries at the 3-21G basis set, they stated [27]: "The hfsc computed... closely mirror the experimental values, except for the slightly larger hfsc predicted for the proton at the 5 (7) -position". However, inspection of their data moreover shows the theoretical value of $a_2^H = 0.0300$ mT (1-*tert*-butylazulene) also to deviate significantly from the experimental $a_2^H = 0.0398$ mT.

Hoping to achieve a better agreement, we applied more sophisticated quantum chemical calculations, first on the unsubstituted azulene radical anion **1**$^{\bullet-}$ itself and on its 6-*tert*-butyl derivative **2**$^{\bullet-}$. The result was, however, rather disappointing. The agreement between theory and experiment could not really be improved by use of the semi-empirical PM3 and PM6 models or by *ab-inito* calculations (DFT, B3LYP 6-31G(p,d) basis set; see Table 3). In fact, it was even worse than the McLachlan results. In particular, the high spin densities ρ_2^π, ρ_4^π, ρ_6^π, and ρ_8^π were calculated significantly lower than the experimental values.

We then turned to the azulene ester radical anions in order to study the effect of electron-withdrawing substituents at the azulene skeleton and also to possibly find out the reasons for several puzzling peculiarities observed in the EPR spectra of certain azulene ester radical anions.

Electron-withdrawing substituents such as ester groups significantly affect the spin density distribution

Table 3. Experimental (Exp: $\rho_\mu^\pi = a_\mu^H / -2.3$) and MO theoretical[a] spin densities.

Radical anion		ρ_1^π	ρ_2^π	ρ_3^π	ρ_4^π	ρ_5^π	ρ_6^π	ρ_7^π	ρ_8^π
	Exp	0.012	0.172	0.012	0.270	0.058	0.384	0.058	0.270
	McL	−0.027	0.120	−0.027	0.292	−0.081	0.368	−0.081	0.292
1$^{\bullet-}$[b]	PM3	0.001	0.113	0.001	0.168	0.018	0.286	0.018	0.168
	PM6	0.001	0.129	0.001	0.154	0.021	0.263	0.020	0.154
	B3L	0.003	0.113	0.003	0.173	0.020	0.277	0.020	0.173
	Exp	–	0.162	< 0.015	0.317	0.086	0.393[d]	0.055	0.256
	McL	−0.031	0.151	−0.016	0.319	−0.096	0.355	−0.061	0.258
6a$^{\bullet-}$[c]	PM3	0.001	0.096	0.000	0.160	0.022	0.294	0.013	0.194
	PM6	0.000	0.105	0.000	0.145	0.027	0.272	0.012	0.188
	B3L	0.002	0.097	0.002	0.175	0.019	0.288	0.020	0.188
	Exp	0.014	–	0.014	0.277	0.074	0.378	0.074	0.277
	McL	0.035	0.056	0.035	0.284	−0.086	0.321	−0.086	0.284
19$^{\bullet-}$	PM3	0.015	0.103	0.015	0.180	0.013	0.276	0.011	0.183
	PM6	0.018	0.109	0.018	0.176	0.012	0.266	0.011	0.178
	B3L	0.014	0.028	0.014	0.180	0.014	0.261	0.014	0.179
	Exp	0.071	0.128	0.038	–	0.017	0.236	0.017	0.190
	McL	−0.035	0.104	−0.028	0.211	−0.023	0.185	0.023	0.126
11a$^{\bullet-}$	PM3	0.006	0.117	0.012	0.228	0.007	0.152	0.072	0.047
	PM6	0.010	0.135	0.010	0.200	0.013	0.122	0.092	0.033
	B3L	0.007	0.115	0.001	0.193	0.012	0.131	0.057	0.060
	Exp	0.013	0.086	0.013	0.153	–	0.358	0.135	0.411
	McL	0.039	0.048	−0.015	0.014	0.007	0.408	−0.105	0.424
12a$^{\bullet-}$	PM3	0.040	0.060	0.013	0.013	0.085	0.269	0.003	0.316
	PM6	0.063	0.042	0.032	0.000	0.115	0.225	0.014	0.318
	B3L	0.025	0.066	0.011	0.033	0.038	0.307	0.007	0.307
	Exp	0.013	0.159	0.013	0.185	0.028	–	0.028	0.185
	McL	−0.033	0.099	−0.033	0.161	0.013	0.205	0.013	0.161
13a$^{\bullet-}$	PM3	0.000	0.115	0.000	0.112	0.046	0.219	0.048	0.105
	PM6	0.000	0.140	0.000	0.092	0.054	0.181	0.056	0.080
	B3L	0.002	0.117	0.002	0.103	0.049	0.182	0.047	0.104

[a] McL = semi-empirical McLachlan approximation; PM3, PM6: see text; B3L = DFT calculation with Becke-3-LYP basis functions; [b] ρ_μ^π (Exp) were taken from ref. [26]; [c] ρ_μ^π (Exp) was calculated from the coupling constants of **8a**$^{\bullet-}$; [d] ρ_6^π (Exp) was calculated from a_6^H of **9**$^{\bullet-}$.

in aromatic radical anions, *e. g.* in the benzene [28], naphthalene [3, 4] and anthracene [29] series. Obviously, this effect is much less pronounced in the radical anions of azulenecarboxylic esters. Inspection of Table 2 shows that the proton hfs coupling constants and thus the corresponding spin densities of many of the ester radical anions are surprisingly close to the values observed for the radical anions of the hydrocarbon azulene **1**$^{\bullet-}$ itself and its alkyl derivatives. This observation is corroborated by the results of our MO theoretical calculations which are compiled in Table 3.

McLachlan-type calculations led to a more or less acceptable agreement with experimental spin densities $\rho_\mu^\pi = a_\mu^H Q^{-1}$ in most cases. The noticeable deviation of one experimentally determined spin density $\rho_4^\pi = a_4^H / -2.3 = 0.153$ of the ethyl azulene-5-carboxylate radical anion (**12a**$^{\bullet-}$) from the MO theoretical value $\rho_4^\pi = 0.013$ is puzzling. The assignment of $a^H = 0.353$ mT to the proton in the 4-position is yet undoubted since it is in agreement with data for **12f**$^{\bullet-}$ and **15**$^{\bullet-}$ and corresponds with data for the unsubstituted azulene radical anion **1**$^{\bullet-}$. Any assignment of $a^H = 0.353$ mT to a proton other than H-4 would lead to even more serious discrepancies.

More sophisticated quantum chemical calculations led to very similar results inclusive of the strange *i. e.* much too low spin density $\rho_4^\pi = 0.000 - 0.014$ in the 4-position of alkyl azulene-5-carboxylate radical anions **12**$^{\bullet-}$ (see Table 3).

First, we determined the optimized geometries of the radical anions by use of DFT-B3LYP type MO cal-

	d(C1–C2) *d*(C2–C3)	*d*(C1–C8a) *d*(C3–C3a)	*d*(C8–C8a) *d*(C3a–C4)	*d*(C7–C8) *d*(C4–C5)	*d*(C6–C7) *d*(C5–C6)	*d*(C3a–C8a)
1$^{\bullet-}$	141.9	141.7	141.1	138.9	142.4	146.7
[a]	*139.9*	*141.8*	*138.3*	*140.6*	*140.3*	*150.1*
6a$^{\bullet-}$	143.2	144.2	144.4	138.9	142.1	144.3
	139.6	142.7	144.6	138.4	142.4	
19$^{\bullet-}$	143.1	140.1	143.6	139.0	142.0	147.3
	142.9	140.2	142.7	139.0	142.0	
11a$^{\bullet-}$	140.5	142.1	142.4	138.1	142.9	147.9
	142.1	141.4	145.9	143.0	138.9	
12a$^{\bullet-}$	143.5	140.4	143.7	140.2	140.1	146.4
	139.7	143.7	144.0	140.2	145.1	
13a$^{\bullet-}$	141.7	141.6	143.0	138.3	143.8	146.2
	141.8	141.5	143.1	138.2	143.8	

Table 4. Calculated bond lengths *d* (pm) in azulene and ethyl azulenecarboxylate radical anions (B3L geometry data).

[a] Bond lengths (*italics*) of azulene (**1**) as determined experimentally by electron diffraction [31].

culations. The resulting bond lengths and bond angles are compiled in Table 4.

The values calculated for **1**$^{\bullet-}$ and **3**$^{\bullet-}$ are in agreement with Waltman and Bargon's theoretical data [27]. They also do not deviate much from X-ray data found for azulene (**1**) [30, 31], azulene-5,7-bis(*N*-butylcarboxamide) and azulene-5,7-bis(*N*-butylcarbothioamide) [32], azulene-1,3-bis(*N*-butylcarboxamide) and azulene-1,3-bis(carboxanilide) [33], and diethyl azulene-1,7-dicarboxylate and diethyl 6-*tert*-butylazulene-1,3-dicarboxylate [34]. In all cases, the calculated bond length *d*(C4–C5)/(C7–C8) (*ca.* 136 – 137 pm) was significantly shorter than the mean value (*ca.* 141 – 144 pm) of the other perimeter bonds. An interesting exception was found for **11a**$^{\bullet-}$, where the perimeter bond next to the ester substituent is significantly elongated (*d*(C4–C5) = 143.7 pm). – The dihedral angles θ between the planes of the azulene and the ester moiety are all close to zero even in the case of **11a**$^{\bullet-}$ where some torsion because of steric repulsion could be expected. As an example, the dependence of the calculated free enthalpy *H* of **19**$^{\bullet-}$ from the torsion angle θ is shown in Fig. 4. Minima due to maximum resonance stabilization occur at $\theta = 0°$ and $\theta = 180°$. An enthalpy maximum is observed for the orthogonal conformation at $\theta = 90°$. The height of the barrier between the two coplanar conformations $\Delta H = 17.7$ kJ mol^{-1} is apparently low enough as to allow free rotation at room temperature and to render the hfs coupling constants a_1^H and a_3^H indistinguishable on the EPR timescale.

Spin densities were then calculated on the basis of these B3L geometries by use of the PM3 and PM6 models as fixed conformation to make spin densities of the various methods more comparable. They are shown in Table 3. As in the case of azulene itself (**1**$^{\bullet-}$), the agreement between the experimental ($\rho_\mu^\pi = a_\mu^H Q^{-1}$) and the theoretical values was again better for the simpler McLachlan type calculations as compared with the more sophisticated semi-empirical PM3 and PM6 results. In fact, the calculations yielded spin densities ρ_μ^π which are too low in nearly all cases and, in particular, in the positions with large experimental coupling constants $a_\mu^H Q^{-1}$. As a consequence, the observed total widths ΔH_{obs} of all EPR spectra are clearly larger than the widths resulting from the sum of the theoretical splittings ΔH_{theor} as calculated by use of the PM3 or PM6 model. For instance, in the case of the ethyl azulene-2-carboxylate radical anion **19**$^{\bullet-}$, $\Delta H_{obs} = \Sigma n_i \cdot a_i^H = 2.606$ mT whereas $\Delta H_{theor} = \Sigma n_i (Q\rho_i^\pi) = 1.831$ mT.

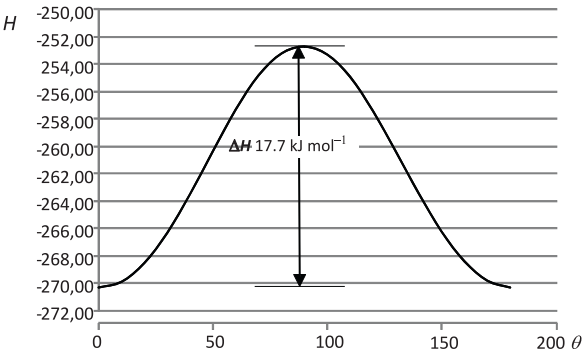


Fig. 4. Dependence of the free enthalpy *H* (kJ mol^{-1}) on the torsion angle θ (deg) between the azulene and the ester plane of the ethyl azulene-2-carboxylate radical anion (**19**$^{\bullet-}$).

The spin density distributions of azulene-1-carboxylate (**6a**$^{\bullet-}$) and azulene-2-carboxylate (**19**$^{\bullet-}$) radical anions furthermore are strikingly similar although of course not fully identical. This is unexpected since the symmetry of **19**$^{\bullet-}$ is the same as of **1**$^{\bullet-}$ whereas the lower symmetry of the 1-isomer **6a**$^{\bullet-}$ should strongly disturb the spin density distribution. Even ester substituents in the high-spin-density 4-position (**11a**$^{\bullet-}$) and 6-position (**13a**$^{\bullet-}$) generate spin density distributions which are very similar.

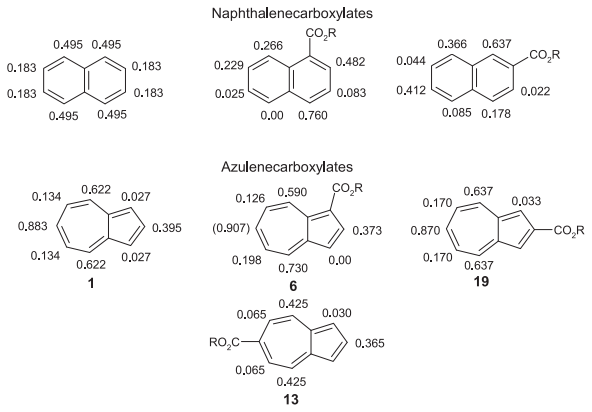
Conclusion

A variety of mostly novel alkyl azulenecarboxylates was prepared by suitable methods.

Their electrochemical behavior as studied by means of differential pulse polarography and cyclovoltammetry revealed a single electron transfer step under formation of persistent radical anions, the EPR spectra of which could be recorded after *in situ* electroreduction. Assignment of the proton hfs coupling constants was possible by use of suitably substituted derivatives and theoretical calculations.

Apparently, the influence of the electron-withdrawing ester substituents on the proton hfs coupling constants of the non-alternant azulene π-electron systems is significantly less pronounced compared with the related derivatives of the alternant naphthalene core (see examples in Scheme 4).

MO calculations of the spin density distribution in azulene ester radical anions led to only moderate agreement with the experimental data as determined from the proton hfs coupling constants by use of the McConnell relationship. This is in accordance with the literature results [26, 27] on the radical anions of azulenes substituted with electron-donating alkyl groups.



Scheme 4. Proton hfs coupling constants a_{μ}^{H} (mT) of alkyl naphthalenecarboxylate and azulenecarboxylate radical anions.

Experimental

Melting points (corrected): Electrothermal. Boiling points were determined during distillation. UV/Vis spectra (solvent EtOH): Hitachi 200 spectrophotometer. NMR spectra (δ in ppm *vs.* Me_4Si; $^1H,^1H$ coupling constants J in Hz) were recorded on WH 270 or WM 400 spectrometers (Bruker) at 250 or 400 MHz (^1H) and 62.9 or 100 MHz (^{13}C) in $CDCl_3$. Assignments were performed by the DEPT method and comparison with theoretical chemical shifts. The ^{13}C NMR spectra of the esters **6a**, **11a**, **12a**, **13a**, **16**, **17** and **19** were calculated by use of the DFT method applying the GAUSSIAN 09 program [35]. The DFT shifts were calculated at the PBE0/6−311+G(2d,p)-SCRF//B3LYP/6−311+G(2d,p) (NMR//GO) level of theory and are linearly scaled. They are averaged over Boltzmann populations of four best conformations (two for **11a**), found by rotating the CO_2Et and *tert*-Bu groups. The NMR spectra of the other esters were calculated by use of the MESTRENOVA 7 program. IR spectra (films for liquids, KBr pellets for solids, ν in cm^{-1}): FT-IR 1720X (Perkin-Elmer) and Genesis-FT-IR (ATI-Mattson). MS: CH 7 (EI, 70 eV, Varian), HRMS: 70-250S (VG-Analytical). Analytical thin layer chromatography (TLC): Al foils coated with SiO_2 $60F_{254}$ (Merck). Preparative scale layer chromatography (PLC): glass plates coated with a 2 mm layer of SiO_2 $60F_{254}$ (Merck). Column chromatography (CC): Kieselgel 60 (70 – 230 mesh, Merck). Analytical GC: GC 4200 (Carlo Erba) equipped with a 50 m fused silica capillary SE 54 column (Macherey & Nagel). Preparative GC: GC-8A (Shimadzu) equipped with a 3-m steel column packed with 15 % SE 30 on Chromosorb WAW and heat conductance detector. Starting temp.: 100 °C, gradient: 3 °C min^{-1} until 250 °C. Up to 30 mg of an azulene mixture could be separated within 8 h.

Differential pulse polarograms were measured with the VA 663/Polarecord 626 (Metrohm); cyclic voltamograms: VA-Scanner E 612 (Metrohm) with plotter Servotec 7040 A (Hewlett Packard). Potentials were measured in DMF-0.1 N tetrapropylammonium bromide (TPAB) by use of a HMDE working cathode *vs.* an internal Ag wire as reference electrode, which corresponds to the Ag/AgBr couple in the TEAB solution [22].

The *in situ* generation of the radical anions in dry DMF at suitable temperatures by use of a Bank Electronic (Wenking type) potentiostat MP 31 and the measurement of the EPR spectra in flat quartz cells have been described ear-

lier [23, 24]. A Bruker ESP 300 E spectrometer was used. Spectra simulations were carried out by using the SIMFONIA program (Bruker).

Starting compounds

Azulene (**1**) is commercially available but expensive (*ca.* 100 Euro per g). We have therefore prepared it according to the procedure of K. Hafner [11], to whom we are also indebted for a generous gift of 12 g of **1** as start-up for our investigations. 6-Methylazulene (**2**) [12], 1-*tert*-butylazulene (**4**) [13], 6-*tert*-butylazulene (**3**) [13], 5-*tert*-butylindane (**14**) [17], and methyl azulene-5-carboxylate (**12d**) [36] were prepared according to the literature procedures.

4,6′-Biazulenyl

A solution of azulene (**1**) (500 mg, 3.90 mmol) in dry Et_2O (25 mL) was dropped into a solution of *tert*-butylmagnesium chloride prepared from Mg (93 mg, mmol) and *tert*-butyl chloride in dry Et_2O (50 mL) under N_2. The mixture was stirred at 20 °C for 10 h and then poured into H_2O (0 °C) with a layer of hexane. After exhaustive extraction with hexane, the solvent was removed under vacuum. The residue was dissolved in benzene and refluxed with chloroanil (2.0 g) for 2 h. Evaporation of the solvent and CC (AcOEt-hexane 1 : 50, $R_f = 0.29$) gave 4,6′-biazulenyl (150 mg, 30 %) as blue crystals. ^{1}H NMR spectrum (400 MHz) and MS were in agreement with lit. [16].

*Ethyl indane-2-carboxylate (**18**)*

Reaction of *indane-2-carboxylic acid* [37] (25.0 g, 0.155 mmol) with EtOH (200 mL) in the presence of conc. H_2SO_4 (1.5 mL) according to a standard laboratory procedure [38] gave **18** (17.8 g, 60 %) as a colorless, viscous liquid. B. p. 113 – 114 °C/1.2 mbar. – IR: $\nu = 3450$, 2981, 1734 (C=O), 1462, 1373, 1171, 1033, 752, 490 cm^{-1}. – ^{1}H NMR: $\delta = 1.30$ (t, $J = 7.1$, 3 H, CH_3), 3.26 (m, 5 H), 4.18 (q, $J = 7.1$, 2 H, OCH_2), 7.18 (m, 4 H, H_{ar}). – ^{13}C NMR: $\delta = 13.8$ (CH_3), 30.4 (C-1/3), 43.2 (C-2), 60.1 (OCH_2), 123.8 (C-4/7), 126.1 (C-5/6), 141.2 (C-3a/7a), 174.8 (C=O).

Alkyl azulenecarboxylates by carbobromination and alcoholysis [18]; General protocol. ***Caution! CCl_4 is carcinogenic! CO is toxic!***

The respective azulene was heated to reflux in CCl_4 under an atmosphere of dry N_2. A solution of oxalyl dibromide (30 % excess) in dry CCl_4 was injected into the boiling solution. Refluxing was continued for 20 min while the color turned from blue to dark red and CO evolved. EtOH or *tert*-BuOH (6 mL mmol^{-1} azulene) was dropped into the warm reaction mixture which was then stirred for another 30 min. The solvents were removed under vacuum. The residue was extracted with hexane and the extract was pre-purified by flash chromatography (SiO_2, AcOEt-hexane 1 : 50).

*Ethyl azulene-1-carboxylate (**6a**) and ethyl 3-bromoazulene-1-carboxylate (**6b**)*

Azulene (**1**) (1.00 g, 7.80 mmol) gave **6a** as a lilac oil [39] (619 mg, 39.6 %) after CC (toluene-hexane 1 : 1, $R_f = 0.13$). – UV/Vis: λ_{max} ($\lg \varepsilon_{max}$) = 192 (4.61), 208 (4.51), 271 (4.72), 281 (4.72), 505 (2.66), 544 (2.59), 601 (2.15) nm. – IR: $\nu = 1688$ (C=O) cm^{-1}. – The ^{1}H NMR spectrum was in agreement with lit. [40]. – ^{13}C NMR: $\delta = 14.2$ (CH_3), 59.3 (OCH_2), 116.7 (C-1), 117.1 (C-3), 126.2 (C-5), 127.1 (C-7), 137.3 (C-8), 137.7 (C-6), 138.5 (C-4), 139.8 (C-2), 140.2 (C-8a), 144.3 (C-3a), 165.0 (C=O). – MS: m/z (%) = 200 (54) $[M]^+$, 172 (14) $[M–C_2H_4]^+$, 155 (100) $[M–OEt]^+$, 128 (32) $[C_{10}H_8]^+$, 127 (38) $[C_{10}H_7]^+$, 126 (16) $[C_{10}H_6]^+$, 115 (4) $[C_9H_7]^+$, 101 (8), 77 (13) $[C_6H_5]^+$. – HRMS: $m/z = 200.0839$ (calcd. 200.0837 for $C_{13}H_{12}O_2$). – $C_{13}H_{12}O_2$ (200.22): calcd. C 77.98, H 6.04; found C 77.27, H 6.26.

In addition, CC (AcOEt-hexane 1 : 40, $R_f = 0.08$) gave **6b** (51.0 mg, 2.3 %) as red-violet crystals. M. p. 64 – 65 °C. – ^{1}H NMR: $\delta = 1.42$ (t, $J = 7.1$, 3 H, CH_3), 4.40 (q, $J = 7.1$, 2 H, OCH_2), 7.47 (t, $J = 9.5$, 1 H, H-5), 7.52 (t, $J = 9.5$, 1 H, H-7), 7.79 (t, $J = 9.5$, 1 H, H-6), 8.30 (s, 1 H, H-2), 8.44 (d, $J = 9.5$, 1 H, H-4), 9.58 (d, $J = 9.5$, 1 H, H-8). – ^{13}C NMR: $\delta = 14.1$ (CH_3), 59.6 (OCH_2), 103.9 (C-3), 115.8 (C-1), 126.6 (C-5), 127.7 (C-7), 137.1 (C-8), 137.7 (C-6), 139.5 (C-4), 139.6 (C-3a), 139.7 (C-2), 140.4 (C-8a), 164.0 (C=O). – MS: m/z (%) = 280 (37) $[M]^+$, 278 (37) $[M]^+$, 252 (18) $[M–C_2H_4]^+$, 250 (19) $[M–C_2H_4]^+$, 235 (53) $[M–OEt]^+$, 233 (54) $[M–OEt]^+$, 208 (16) $[M–CO_2Et]^+$, 207 (14), 206 (18) $[M–CO_2Et]^+$, 205 (15), 127 (18) $[C_{10}H_7]^+$, 126 (100) $[C_{10}H_6]^+$, 125 (11), 76 (14), 75 (13), 63 (18). – HRMS: $m/z = 277.9909$ (calcd. 277.9942 for $C_{13}H_{11}^{79}BrO_2$).

*Ethyl 6-methylazulene-1-carboxylate (**7**)*

6-Methylazulene (**2**) [12] (1.00 g, 7.00 mmol) gave **7** as lilac crystals (640 mg, 42.4 %) after CC (toluene-hexane 1 : 1, $R_f = 0.13$). M. p. 51 – 53 °C. – IR: $\nu = 1684$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.41$ (t, $J = 7.1$, 3 H, CH_3), 2.69 (s, 3 H, CH_3), 4.39 (q, $J = 7.1$, 2 H, OCH_2), 7.18 (d, $J = 4.1$, 1 H, H-3), 7.31 (d, $J = 9.9$, 1 H, H-5), 7.42 (d, $J = 10.2$, 1 H, H-7), 8.24 (d, $J = 4.1$, 1 H, H-2), 8.28 (d, $J = 9.9$, 1 H, H-4), 9.47 (d, $J = 10.2$, 1 H, H-8). – ^{13}C NMR: $\delta = 14.2$ (CH_2CH_3), 27.6 (6-CH_3), 59.2 (OCH_2), 116.6 (C-1), 117.0 (C-3), 127.7 (C-7), 128.6 (C-5), 136.4 (C-2), 136.8 (C-4), 138.3 (C-8), 138.9 (C-3a), 142.8 (C-8a), 150.7 (C-6), 165.1 (C=O). – MS: m/z (%) = 214 (45)

$[M]^+$, 186 (12) $[M–C_2H_4]^+$, 170 (14), 169 (100) $[M–OEt]^+$, 142 (33) $[C_{11}H_{10}]^+$, 139 (16) $[C_{11}H_7]^+$, 115 (31), $[C_9H_7]^+$. – HRMS: $m/z = 214.0985$ (calcd. 214.0994 for $C_{14}H_{14}O_2$).

*Ethyl 6-tert-butylazulene-1-carboxylate (**8a**)*

6-*tert*-Butylazulene (**3**) [13] (500 mg, 2.71 mmol) gave **8a** as a red-violet oil (328 mg, 47.1 %) after CC (toluene-hexane 1 : 1, $R_f = 0.25$). – IR: $\nu = 1682$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.41$ (t, $J = 7.1$, 3 H, CH_3), 1.45 (s, 9 H, CH_3), 4.41 (q, $J = 7.1$, 2 H, OCH_2), 7.18 (d, $J = 4.1$, 1 H, H-3), 7.59 (dd, $J = 10.2/1.5$, 1 H, H-5), 7.73 (dd, $J = 10.6/1.5$, 1 H, H-7), 8.27 (d, $J = 4.1$, 1 H, H-2), 8.37 (d, $J = 10.2$, 1 H, H-4), 9.54 (d, $J = 10.6$, 1 H, H-8). – ^{13}C NMR: $\delta = 14.2$ (CH_3), 31.4 (C(CH_3)$_3$), 38.3 (C(CH_3)$_3$), 59.2 (OCH_2), 116.2 (C-1), 116.5 (C-3), 124.4 (C-5), 125.3 (C-7), 136.3 (C-2), 136.7 (C-4), 138.8 (C-8), 139.1 (C-3a), 143.1 (C-8a), 162.8 (C-6), 165.2 (C=O). – MS: m/z (%) = 256 (100) $[M]^+$, 241 (11) $[M–CH_3]^+$, 213 (13), 211 (71) $[M–OEt]^+$, 196 (14), 195 (14), 184 (53), 169 (20), 168 (20), 167 (17), 153 (38), 152 (39), 141 (15), 128 (19) $[C_{10}H_8]^+$, 127 (13), 126 (15), 115 (24), $[C_9H_7]^+$, 91 (4) $[C_7H_7]^+$. – $C_{17}H_{20}O_2$ (256.34): calcd. C 79.65, H 7.84; found C 77.49, H 7.89.

*tert-Butyl 6-tert-butylazulene-1-carboxylate (**8b**)*

6-*tert*-Butylazulene (**3**) [13] (500 mg, 2.71 mmol) gave **8b** as a semisolid violet oil (114 mg, 14.8 %) after CC (toluene-hexane 1 : 1, $R_f = 0.34$). – IR: $\nu = 1686$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.40$ (s, 9 H, CH_3), 1.60 (s, 9 H, CH_3), 7.10 (d, $J = 4.1$, 1 H, H-3), 7.51 (dd, $J = 10.2/1.5$, 1 H, H-5), 7.62 (dd, $J = 10.6/1.5$, 1 H, H-7), 8.16 (d, $J = 4.1$, 1 H, H-2), 8.30 (d, $J = 10.2$, 1 H, H-4), 9.44 (d, $J = 10.7$, 1 H, H-8). – ^{13}C NMR: $\delta = 28.2$ (CC(CH_3)$_3$), 31.5 (CC(CH_3)$_3$), 38.3 (CC(CH_3)$_3$), 79.2 (OC(CH_3)$_3$), 116.2 (C-3), 117.7 (C-1), 124.1 (C-5), 125.0 (C-7), 136.2 (C-2), 136.6 (C-4), 138.7 (C-3a), 139.1 (C-8), 142.9 (C-8a), 162.6 (C-6), 164.8 (C=O). – MS: m/z (%) = 284 (14) $[M]^+$, 229 (17) 228 (100) $[M–C_4H_8]^+$, 213 (33), 211 (10), 184 (12), 169 (12), 167 (9), 153 (12), 152 (12), 141 (10), 129 (8), 128 (10) $[C_{10}H_8]^+$, 115 (8) $[C_9H_7]^+$, 85 (18), 83 (30), 56 (8) $[C_4H_8]^+$.

*Ethyl 3-tert-butylazulene-1-carboxylate (**9**)*

1-*tert*-Butylazulene (**4**) [13] (680 mg, 3.70 mmol) gave **9** as a blue-violet oil (162 mg, 17.0 %) after CC (AcOEt-hexane 1 : 50, $R_f = 0.80$). – IR: $\nu = 1733$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.44$ (t, $J = 7.1$, 3 H, CH_3), 1.58 (s, 9 H, C(CH_3)$_3$), 4.42 (q, $J = 7.1$, 2 H, OCH_2), 7.35 (t, $J = 9.9$, 1 H, H-5), 7.44 (t, $J = 9.9$, 1 H, H-7), 7.72 (t, $J = 9.9$, 1 H, H-6), 8.29 (s, 1 H, H-2), 8.78 (d, $J = 10.2$, 1 H, H-4), 9.64 (d, $J = 10.2$, 1 H, H-8). – ^{13}C NMR: $\delta = 14.3$ (CH_2CH_3), 31.4 (C(CH_3)$_3$), 32.7 (C(CH_3)$_3$), 59.2 (OCH_2), 114.2 (C-1), 124.4 (C-5), 126.6 (C-7), 136.5 (C-8), 136.8 (C-6), 138.05 (C-4), 138.15 (C-2), 138.21 (C-3a), 139.5 (C-3), 141.8 (C-8a), 165.1 (C=O) cm^{-1}. – MS: m/z (%) = 256 (36) $[M]^+$, 242 (16), 241 (100) $[M–CH_3]^+$, 213 (16), 211 (6) $[M–OEt]^+$, 153 (6), 152 (7).

*Ethyl 3,6-di-tert-butylazulene-1-carboxylate (**10a**)*

Friedel-Crafts *tert*-butylation of 6-*tert*-butylazulene (**3**) [13] (500 mg, 2.70 mmol) subsequent carbobromination without isolation of the intermediate 1,6-di-*tert*-butylazulene (**5**), and ethanolysis gave (**10a**) as violet crystals (80 mg, 9.5 %) after CC (toluene-hexane 1 : 1). M. p. 69 – 72 °C. – IR: $\nu = 1688$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.42$ (t, $J = 7.1$, 3 H, CH_3), 1.46 (s, 9 H, C(CH_3)$_3$), 1.57 (s, 9 H, C(CH_3)$_3$), 4.40 (q, $J = 7.1$, 2 H, OCH_2), 7.53 (dd, $J = 10.7/2.0$, 1 H, H-5), 7.61 (dd, $J = 10.7/2.0$, 1 H, H-7), 8.18 (s, 1 H, H-2), 8.72 (d, $J = 10.7$, 1 H, H-4), 9.53 (d, $J = 10.7$, 1 H, H-8). – ^{13}C NMR: $\delta = 14.3$ (CH_2CH_3), 31.4 (2 C(CH_3)$_3$), 32.6 (6-C(CH_3)$_3$), 38.1 (3-C(CH_3)$_3$), 59.1 (OCH_2), 113.6 (C-1), 122.6 (C-5), 124.8 (C-7), 135.7 (C-8), 135.8 (C-4), 136.9 (C-2), 137.8 (C-3), 138.3 (C-3a), 140.6 (C-8a), 162.4 (C-6), 165.2 (C=O). – MS: m/z (%) = 312 (29) $[M]^+$, 298 (20), 297 (100) $[M–CH_3]^+$, 269 (5), 267 (7) $[M–OEt]^+$, 87 (7), 85 (58), 83 (70), 71 (14), 57 (24) $[C_4H_9]^+$.

*tert-Butyl 3,6-di-tert-butylazulene-1-carboxylate (**10b**)*

The *tert*-butyl ester **10b** was prepared from **3** [13] *via* **5** (500 mg, 2.70 mmol) as described for **10a** by use of *tert*-BuOH instead of EtOH. CC (toluene-hexane 1 : 1, $R_f = 0.37$) gave **10b** as violet crystals (36 mg, 2 %). M. p. 127 – 130 °C. – IR: $\nu = 1727$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.46$ (s, 9 H, C(CH_3)$_3$), 1.56 (s, 9 H, C(CH_3)$_3$), 1.65 (s, 9 H, OC(CH_3)$_3$), 7.50 (dd, $J = 10.7/2.0$, 1 H, H-5), 7.57 (dd, $J = 10.7/2.0$, 1 H, H-7), 8.12 (s, 1 H, H-2), 8.70 (d, $J = 10.7$, 1 H, H-4), 9.49 (d, $J = 10.7$, 1 H, H-8). – ^{13}C NMR: $\delta = 28.2$ (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 31.5 (C(CH_3)$_3$), 32.6 (6-C(CH_3)$_3$), 38.0 (3-C(CH_3)$_3$), 79.2 (OC(CH_3)$_3$), 115.3 (C-1), 122.2 (C-5), 124.5 (C-7), 135.6 (C-8), 135.8 (C-4), 137.2 (C-2), 137.5 (C-3), 138.1 (C-3a), 140.1 (C-8a), 162.1 (C-6), 164.9 (C=O). – MS: m/z (%) = 340 (36) $[M]^+$, 284 (30) $[M–C_4H_8]^+$, 270 (18), 269 (100), 225 (26), 57 (18) $[C_4H_9]^+$, 56 (24) $[C_4H_8]^+$.

Alkyl azulenecarboxylates by ring enlargement of indanes [20, 36]

Caution! Diazomethane is toxic, carcinogenic and explosive! Also the less hazardous alkyl diazoacetates should be handled with care. All reactions with these reagents must therefore be performed behind a protective shield in a well ventilated hood.

*Ethyl azulenene-2-carboxylate (**19**)*

The ester **18** (4.00 g, 21 mmol) was dissolved in cyclohexane (20 mL) and heated to 80 °C. Five 10 mL portions of a diazomethane solution [38] (30 mmol in total) in cyclohexane were dropped in slowly (*ca.* 1 drop s^{-1}) so that the concentration of the diazomethane was low at any time. The progress of the reaction was monitored by drawing small samples after the addition of each portion, reaction with chloranil in a test tube, and controlling by TLC (AcOEt-hexane 1 : 5). Finally, the solvent was removed under vacuum. The residue was dehydrogenated with chloranil as described below. CC (toluene-hexane 1 : 1 $R_f = 0.33$) gave **19** (57 mg, 1.4 %) as blue needles. – UV/Vis: λ_{max} (lg ε_{max}) = 200 (4.31), 239 (4.40), 263 (4.68), 273 (0.69), 278 (4.78), 287 (4.66), 326 (3.66), 336 (3.05), 348 (3.59), 558 (2.41), 590 (2.54), 631 (2.56), 685 (2.26) nm. – ^{1}H NMR and ^{13}C NMR spectra were in agreement with lit. [21]. – MS: m/z (%) = 200 (59) $[M]^+$, 172 (22), $[M–C_2H_4]^+$, 156 (19), 155 (58), $[M–OEt]^+$, 128 (100) $[C_{10}H_8]^+$, 127 (67) $[C_{10}H_7]^+$, 126 (25), 77 (23) $[C_6H_5]^+$. – HRMS: m/z = 200.0839 (calcd. 200.0837 for $C_{13}H_{12}O_2$).

Reaction of indanes with alkyl diazoacetates and subsequent dehydrogenation

Ethyl diazoacetate [41] or *tert*-butyl diazoacetate [42] was dropped into an excess of the respective indane derivative with stirring under N_2 at 20 °C. The mixture was heated to 140 °C for 6 h. The excessive indane was distilled off under vacuum. The residue (hydroazulene) was dissolved in a tenfold amount of benzene and refluxed with an equimolar amount of chloranil for 2 h. The color changed from yellow to green-blue. The solvent was removed under vacuum, and the residue was extracted with hexane in a Soxhlet apparatus. Flash-CC (toluene-hexane 1 : 1) of the extract yielded the deeply blue azulene (mixture), which was further purified by suitable chromatographic methods.

Reaction of indane (106 g, 0.90 mol) with ethyl diazoacetate (53.4 g, 468 mmol) led to a mixture of ethyl azulene-4-carboxylate (**11a**), ethyl azulene-5-carboxylate (**12a**), ethyl azulene-6-carboxylate (**13a**), and ethyl 1-chloroazulene-5-carboxylate (**12c**). The components were separated by repeated CC and prep. GC.

Ethyl azulene-4-carboxylate (***11a***): $R_f = 0.38$ (toluene-hexane 1 : 2, then AcOEt-hexane 1 : 50), blue liquid (1.50 g, 1.5 %). – IR: $\nu = 1722$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.47$ (t, $J = 7.1$, 3 H, CH_3), 4.54 (q, $J = 7.1$, 2 H, OCH_2), 7.24 (t, $J = 9.7$, 1 H, H-7), 7.46 (d, $J = 3.8$, 1 H, H-1), 7.49 (d, $J = 9.7$, 1 H, H-5), 7.63 (t, $J = 9.7$, 1 H, H-6), 7.77 (d, $J = 3.8$, 1 H, H-3), 8.00 (t, $J = 3.8$, 1 H, H-2), 8.38 (d, $J = 9.7$, 1 H, H-8). – ^{13}C NMR: $\delta = 13.9$ (CH_3), 61.5 (OCH_2), 117.4 (C-3), 119.2 (C-1), 122.2 (C-5), 123.8 (C-7), 134.7 (C-3a), 135.8 (C-6), 136.5 (C-8), 137.3 (C-4), 138.4 (C-2), 142.4 (C-8a), 169.1 (C=O). – MS: m/z (%) = 201 (9), 200 (86) $[M]^+$, 172 (36) $[M–C_2H_4]^+$, 155 (11) $[M–OEt]^+$, 144 (9), 129 (8), 128 (100) $[C_{10}H_8]^+$, 127 (61) $[C_{10}H_7]^+$, 126 (32), 116 (20), 115 (43) $[C_9H_7]^+$, 101 (13), 77 (24) $[C_6H_5]^+$. – HRMS: m/z = 200.0840 (calcd. 200.0837 for $C_{13}H_{12}O_2$).

Ethyl azulene-5-carboxylate (***12a***): $R_f = 0.39$ (2 × toluene-hexane 1 : 2), violet needles (6.51 g, 6.9 %). M. p. 35 – 37 °C (lit. [36]: 30 – 31 °C). – UV/Vis: λ_{max} (lg ε_{max}) = 209 (5.05), 279 (5.31), 288 (5.23), 503 (2.20), 524 (2.35), 543 (2.43), 558 (2.52), 579 (2.47), 607 (2.48), 632 (2. 19), 667 (2.10) nm, in agreement with lit. [38]. – IR: $\nu = 1707$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.44$ (t, $J = 7.1$, 3 H, CH_3), 4.44 (q, $J = 7.1$, 2 H, OCH_2), 7.19 (t, $J = 9.2$, 1 H, H-7), 7.51 (d, $J = 3.6$, 1 H, H-1), 7.64 (d, $J = 3.6$, 1 H, H-3), 7.93 (t, $J = 3.6$, 1 H, H-2), 8.39 (d, $J = 9.2$, 1 H, H-6), 8.49 (d, $J = 9.7$, 1 H, H-8), 9.20 (d, $J = 1.6$, 1 H, H-4). – ^{13}C NMR: $\delta = 14.0$ (CH_3), 61.2 (OCH_2), 121.0 (C-1), 121.6 (C-3), 122.9 (C-5), 123.3 (C-7), 137.0 (C-4), 137.1 (C-2), 137.3 (C-8a), 137.5 (C-6), 138.7 (C-8), 139.2 (C-3a), 167.8 (C=O). – MS: m/z (%) = 201 (12), 200 (100) $[M]^+$, 173 (14), 172 (94) $[M–C_2H_4]^+$, 155 (54) $[M–OEt]^+$, 128 (14) $[C_{10}H_8]^+$, 127 (76) $[C_{10}H_7]^+$, 126 (32), 115 (14) $[C_9H_7]^+$, 101 (10), 77 (22) $[C_6H_5]^+$. – $C_{13}H_{12}O_2$ (200.24): calcd. C 77.98, H 6.04; found C 77.72, H 6.25.

Ethyl azulene-6-carboxylate (***13a***): $R_f = 0.49$ (2 × toluene-hexane 1 : 2, then prep. GC), blue-green needles (2.19 g, 2.3 %). M. p. 76 °C [43]. – UV/Vis: λ_{max} (lg ε_{max}) = 211 (4.70), 280 (4.68), 334 (3.49), 352 (3.24), 380 (1.22), 625 (2.09), 680 (2.10), 757 (1.51) nm. – IR: $\nu = 1708$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.43$ (t, $J = 7.1$, 3 H, CH_3), 4.43 (q, $J = 7.1$, 2 H, OCH_2), 7.43 (d, $J = 4.0$, 2 H, H-1/3), 8.02 (t, $J = 4.0$, 1 H, H-2), 8.03 (d, $J = 10.7$, 2 H, H-5/7), 8.40 (d, $J = 10.7$, 2 H, H-4/8). – ^{13}C NMR: $\delta = 13.9$ (CH_3), 61.6 (OCH_2), 118.5 (C-1/3), 122.6 (C-5/7), 134.4 (C-2), 136.0 (C-6), 139.7 (C-4/8), 140.9 (C3a/8a), 167.8 (C=O). – MS: m/z (%) = 201 (14), 200 (82) $[M]^+$, 173 (14), 172 (100) $[M–C_2H_4]^+$, 155 (13) $[M–OEt]^+$, 128 (16) $[C_{10}H_8]^+$, 127 (70) $[C_{10}H_7]^+$, 126 (34), 116 (8), 115 (25) $[C_9H_7]^+$, 101 (11), 77 (20) $[C_6H_5]^+$. – HRMS: m/z = 200.0844 (calcd. 200.0837 for $C_{13}H_{12}O_2$).

Ethyl 1-chloroazulene-5-carboxylate (***12c***), $R_f = 0.39$ (2 × toluene-hexane 1 : 2, then prep. GC), blue-green oil (5 mg, trace). – IR: $\nu = 1708$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.50$ (t, $J = 7.1$, 3 H, CH_3), 4.41 (q, $J = 7.1$, 2 H, OCH_2), 7.17 (t, $J = 10.4$, H-7), 7.52 (d, $J = 4.0$, 1 H, H-3), 7.75 (d, $J = 4.0$, 1 H, H-2), 8.41 (d, $J = 10.4$, 2 H, H-6), 8.51 (d, $J = 10.4$, 1 H, H-8), 9.07 (s, 1 H, H-4). – ^{13}C NMR: $\delta = 14.0$ (CH_3), 61.4 (OCH_2), 120.5 (C-1), 120.8 (C-3), 121.0 (C-7), 123.4 (C-5), 135.1 (C-4), 136.5 (C-8a), 136.8 (C-2), 137.8 (C-8), 139.3 (C-6), 141.1 (C-3a), 167.3 (C=O).

Reaction of 5-*tert*-butylindane (**14**) (3.72 g, 21.4 mmol) with ethyl diazoacetate (53.4 g, 468 mmol) led to a mixture of ethyl 7-*tert*-butylazulene-5-carboxylate (**15**), ethyl 6-*tert*-butylazulene-4-carboxylate (**16**) and ethyl 7-*tert*-butylazulene-4-carboxylate (**17**) which were separated by repeated CC (AcOEt-hexane 1 : 30).

Ethyl 7-tert-butylazulene-5-carboxylate (***15***): $R_f = 0.44$, violet oil (165 mg, 2.8 %). – IR: $\nu = 1708$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.46$ (t, $J = 7.1$, 3 H, CH_3), 1.50 (s, 9 H, $C(CH_3)_3$), 4.46 (q, $J = 7.1$, 2 H, OCH_2), 7.44 (d, $J = 3.6$, 1 H, H-1), 7.55 (d, $J = 3.6$, 1 H, H-3), 7.88 (t, $J = 3.6$, 1 H, H-2), 8.64 (s, 1 H, H-6), 8.76 (s, 1 H, H-8), 9.13 (s, 1 H, H-4). – ^{13}C NMR: $\delta = 14.0$ (CH_2CH_3), 31.5 ($C(CH_3)_3$), 37.3 ($C(CH_3)_3$), 61.2 (OCH_2), 121.1 (C-1), 121.8 (C-5), 122.0 (C-3), 134.8 (C-6), 135.7 (C-2), 136.6 (C-8a), 136.7 (C-8), 137.9 (C-4), 138.9 (C-3a), 142.8 (C-7), 168.4 (C=O). – MS: m/z (%) = 256 (86) $[M]^+$, 241 (100) $[M–CH_3]^+$, 213 (20), 167 (17), 153 (28), 152 (30), 129 (18), 128 (20) $[C_{10}H_8]^+$, 115 (18) $[C_9H_7]^+$, 91 (6) $[C_7H_7]^+$, 77 (8) $[C_6H_5]^+$, 57 (38) $[C_4H_9]^+$. – HRMS: $m/z = 256.1413$ (calcd. 256.1463 for $C_{17}H_{20}O_2$).

Ethyl 6-tert-butylazulene-4-carboxylate (***16***): $R_f = 0.41$, blue oil (517 mg, 9.4 %). – IR: $\nu = 1723$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.45$ (s, 9 H, $C(CH_3)_3$), 1.49 (t, $J = 7.1$, 3 H, CH_3), 4.45 (q, $J = 7.1$, 2 H, OCH_2), 7.36 (d, $J = 4.0$, 1 H, H-1), 7.40 (dd, $J = 10.0/2.0$, 1 H, H-7), 7.61 (d, $J = 4.0$, 1 H, H-3), 7.76 (d, $J = 2.0$, 1 H, H-6), 7.88 (t, $J = 4.0$, 1 H, H-2), 8.31 (d, $J = 10.0$, 1 H, H-8). – ^{13}C NMR: $\delta = 13.9$ (CH_2CH_3), 31.4 ($C(CH_3)_3$), 38.4 ($C(CH_3)_3$), 61.4 (OCH_2), 116.8 (C-3), 118.6 (C-1), 120.7 (C-5), 121.6 (C-7), 133.4 (C-3a), 135.6 (C-8), 136.6 (C-4), 137.3 (C-2), 140.9 (C-8a), 159.7 (C-6), 169.8 (C=O). – MS: m/z (%) = 256 (54) $[M]^+$, 242 (18), 241 (100) $[M–CH_3]^+$, 215 (32), 213 (22), 169 (12), 168 (22), 167 (21), 152 (24), 151 (25), 141 (15), 128 (11) $[C_{10}H_8]^+$, 115 (10) $[C_9H_7]^+$, 57 (17) $[C_4H_9]^+$.

Ethyl 7-tert-butylazulene-4-carboxylate (***17***): $R_f = 0.38$, blue oil (582 mg, 10.7 %). – IR: $\nu = 1723$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.46$ (t, $J = 7.1$, 3 H, CH_3), 1.46 (s, 9 H, $C(CH_3)_3$), 4.51 (q, $J = 7.1$, 2 H, OCH_2), 7.37 (dd, $J = 4.0/1.5$, 1 H, H-1), 7.53 (d, $J = 10.7$, 1 H, H-5), 7.73 (d, $J = 4.0$, 1 H, H-3), 7.76 (dd, $J = 10.7/2.0$, 1 H, H-6), 7.94 (t, $J = 4.0$, 1 H, H-2), 8.59 (d, $J = 2.0$, 1 H, H-8). – ^{13}C NMR: $\delta = 13.9$ (CH_2CH_3), 31.3 ($C(CH_3)_3$), 36.9 ($C(CH_3)_3$), 61.3 (OCH_2), 116.5 (C-3), 118.8 (C-1), 121.9 (C-5), 132.6 (C-6), 133.9 (C-3a), 135.2 (C-4), 135.6 (C-8), 138.1 (C-2), 142.5 (C-8a), 146.1 (C-7), 169.0 (C=O). – MS: m/z (%) = 256 (100) $[M]^+$, 241 (11) $[M–CH_3]^+$, 228 (14) $[M–C_2H_4]^+$, 213 (45), 211 (7), 184 (34), 169 (55), 168 (50), 152 (36), 141 (13), 115 (26) $[C_9H_7]^+$, 77 (5) $[C_6H_5]^+$, 57 (8) $[C_4H_9]^+$. – HRMS: $m/z = 256.1443$ (calcd. 256.1463 for $C_{17}H_{20}O_2$).

Reaction of indane (99 g, 0.84 mol) with *tert*-butyl diazoacetate (43.0 g, 302 mmol) led to a mixture of *tert*-butyl azulene-4-carboxylate (**11b**), *tert*-butyl azulene-5-carboxylate (**12b**) and *tert*-butyl azulene-6-carboxylate (**13b**). The components were separated by repeated CC (3 × toluene-hexane 1 : 2).

tert-Butyl azulene-4-carboxylate (***11b***): $R_f = 0.51$, blue oil (900 mg, 1.3 %). – IR: $\nu = 1721$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.77$ (s, 9 H, $OC(CH_3)_3$), 7.24 (t, $J = 9.7$, 1 H, H-7), 7.39 (d, $J = 9.7$, 1 H, H-5), 7.43 (d, $J = 4.0$, 1 H, H-1), 7.62 (t, $J = 9.7$, 1 H, H-6), 7.79 (d, $J = 3.6$, 1 H, H-3), 7.97 (t, $J = 3.6$z, 1 H, H-2), 8.37 (d, $J = 9.7$, 1 H, H-8). – ^{13}C NMR: $\delta = 27.8$ ($C(CH_3)_3$), 82.4 ($OC(CH_3)_3$), 117.1 (C-3), 119.0 (C-1), 121.9 (C-5), 123.4 (C-7), 134.6 (C-3a), 136.0 (C-6), 136.5 (C-8), 137.9 (C-2), 139.2 (C-4), 142.3 (C-8a), 168.4 (C=O). – MS: m/z (%) = 228 (10) $[M]^+$, 173 (13), 172 (100) $[M–C_4H_8]^+$, 155 (10) $[M–OC(CH_3)_3]^+$, 144 (13), 128 (21) $[C_{10}H_8]^+$, 127 (46) $[C_{10}H_7]^+$, 126 (20), 116 (32), 115 (44) $[C_9H_7]^+$, 101 (10), 77 (20) $[C_6H_5]^+$, 57 (30) $[C_4H_9]^+$. – HRMS: $m/z = 228.1150$ (calcd. 228.1150 for $C_{15}H_{16}O_2$).

tert-Butyl azulene-5-carboxylate (***12b***): $R_f = 0.64$, violet oil (1.75 g, 2.5 %). – IR: $\nu = 1704$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.65$ (s, 9 H, $OC(CH_3)_3$), 7.17 (t, $J = 9.2$, 1 H, H-7), 7.49 (d, $J = 3.6$, 1 H, H-1), 7.62 (d, $J = 3.6$, 1 H, H-3), 7.92 (t, $J = 3.6$, 1 H, H-2), 8.37 (d, $J = 9.2$, 1 H, H-6), 8.45 (d, $J = 10.2$, 1 H, H-8), 9.16 (s, 1 H, H-4). – ^{13}C NMR: $\delta = 27.8$ ($C(CH_3)_3$), 81.1 ($C(CH_3)_3$), 120.9 (C-1), 121.2 (C-3), 122.9 (C-5), 124.4 (C-7), 134.4 (C-4), 136.9 (C-2), 137.3 (C-8a), 137.4 (C-6), 138.5 (C-8), 139.2 (C-3a), 166.9 (C=O). – MS: m/z (%) = 228 (8) $[M]^+$, 173 (12), 172 (100) $[M–C_4H_8]^+$, 155 (14) $[M–OC(CH_3)_3]^+$, 127 (34) $[C_{10}H_7]^+$, 126 (17) $[C_{10}H_7]^+$, 115 (12) $[C_9H_7]^+$, 77 (9) $[C_6H_5]^+$. – HRMS: $m/z = 228.1150$ (calcd. 228.1150 for $C_{15}H_{16}O_2$).

tert-Butyl azulene-6-carboxylate (***13b***): $R_f = 0.75$, blue-green crystals (374 mg, 0.5 %). M. p. 70 – 72 °C. – IR: $\nu = 1711$ (C=O) cm^{-1}. – ^{1}H NMR: $\delta = 1.63$ (s, 9 H, $OC(CH_3)_3$), 7.42 (d, $J = 4.1$, 2 H, H-1/3), 7.97 (d, $J = 10.7$, 2 H, H-5/7), 8.00 (t, $J = 4.1$, 1 H, H-2), 8.38 (d, $J = 10.7$, 2 H, H-4/8). – ^{13}C NMR: $\delta = 27.8$ ($C(CH_3)_3$), 81.7 ($C(CH_3)_3$), 118.2 (C-1/C-3), 122.5 (C-5/C-7), 134.3 (C-2), 137.6 (C-6), 139.3 (C-4/C-8), 140.8 (C3a/C-8a), 166.8 (C=O). – MS: m/z (%) = 228 (10) $[M]^+$, 206 (6), 173 (12), 172 (100) $[M–C_4H_8]^+$, 155 (8) $[M–OC(CH_3)_3]^+$, 143 (6), 127 (28) $[C_{10}H_7]^+$, 126 (14), 115 (12) $[C_9H_7]^+$, 77 (6) $[C_6H_5]^+$, 57 (8) $[C_4H_9]^+$. – HRMS: $m/z = 228.1157$ (calcd. 228.1150 for $C_{15}H_{16}O_2$).

*Ethyl 1,3-dideuteroazulene-4-carboxylate (**11c**)*

The ester **11a** (70 mg, 0.35 mmol) and D_2SO_4 (500 mg) were shaken under N_2 until the color of the solution disappeared. The mixture was covered with a layer of dry hexane (20 mL) and cooled to 5 °C. D_2O (2 – 3 mL) was added

and the blue color reappeared. After the addition of solid NaCl, the ester dissolved in the hexane phase. It was separated, washed with a small amount of D_2O and dried over K_2CO_3. The solvent was removed under vacuum. The product exhibited a degree of deuteration of 50 %. Repetition of the procedure yielded **11c** (52 mg, 74 %, > 99 % deuteration) as a blue oil. The ^{1}H and ^{13}C NMR spectra of **11c** and **11a** agreed with each other except that expectedly the signals at $\delta = 7.46$ (H-1) and 7.77 (H-3) in the ^{1}H NMR spectrum of **11a** were missing for **11c** and the triplet of **11a** at $\delta = 7.99$ (H-2) collapsed into a singlet.

Methyl 1,3-dideuteroazulene-5-carboxylate (***12e***) was prepared from **12d** [36] (100 mg, 0.54 mmol) as described for **11c**. Yield: 47 mg (46 %, > 99 % deuteration), violet crystals. ^{1}H NMR: $\delta = 3.97$ (s, 3 H, OCH_3), 7.17 (dd, $J = 10.7/9.2$, 1 H, H-7), 7.92 (s, 1 H, H-2), 8.37 (d, $J = 9.2$, 1 H, H-6), 8.47 (d, $J = 10.7$, 1 H, H-8), 9.19 (d, $J = 1.5$, 1 H, H-4). – ^{13}C NMR: $\delta = 52.3$ (OCH_3), 121.0 (C-1), 121.7 (C-3), 122.5 (C-5), 123.4 (C-7), 137.0 (C-4), 137.1 (C-2), 137.2 (C-8a), 137.5 (C-6), 138.7 (C-8), 139.1 (C-3a), 168.3 (C=O). – MS: m/z (%) = 189 (10), 188 (100) $[M]^+$, 187 (90), 186 (22), 157 (56) $[M–OCH_3]^+$, 156 (50), 155 (10), 129 (80) $[C_{10}H_6D_2]^+$, 128 (94) $[C_{10}H_5D_2]^+$, 127 (44) $[C_{10}H_7]^+$, 116 (7) $[C_9H_6D]^+$, 102 (11), 101 (8), 78 (18) $[C_6H_4D]^+$, 77 (15) $[C_6H_5]^+$.

Ethyl 1,3-dideuteroazulene-5-carboxylate (***12f***) was prepared from **12a** (30 mg, 0.15 mmol) as described for **11c**. Yield: 25 mg (82 %, > 99 % deuteration), violet crystals. The ^{1}H and ^{13}C NMR spectra of **12a** and **12f** agreed with each other except that expectedly the doublets at $\delta = 7.51$ (H-1) and 7.64 (H-3) in the ^{1}H NMR spectrum of **12a** were missing for **12f** and the triplet of **12a** at $\delta = 7.92$ (H-2) collapsed into a singlet.

Quantum-chemical calculations

DFT calculations of the NMR spectra [44] were performed at the Vuori supercluster of the Finnish IT Center for Science (CSC), *cf.* http://www.csc.fi/english/research/Computing_services/computing.

HMO and McLachlan-type MO calculations were performed by use of an unpublished Fortran-77 program HUECKEL 88 [45, 46]. Semi-empirical PM6 and PM3-type MO calculations were performed by use of the program packages MOPAC 2009 and MOPAC 2012 [47]. DFT-based geometry optimizations and spin density calculations were performed by the B3LYP method [48, 49] with 6-31G(p,d) basis sets. The FIREFLY program [50] was used for the DFT calculations. The QCPE programs DRAW and JMOL (Open Project; http://sourceforge.net/projects/jmol/) were used for the graphical presentation of the results. A conventional PC (Pentium Dual Core CPU E5200, 2.5 GHz; 3.25 GB RAM) was used for the calculations.

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