Synthesis and Properties of Vinylogous 6-(Cyclopentadienyl)pentafulvenes

Matthias Eiermann, Bernd Stowasser [+], Klaus Hafner*, Klaus Bierwirth, Anette Frank, Alexander Lerch, and Jürgen Reußwig

Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstraße 22, D-6100 Darmstadt, F.R.G.

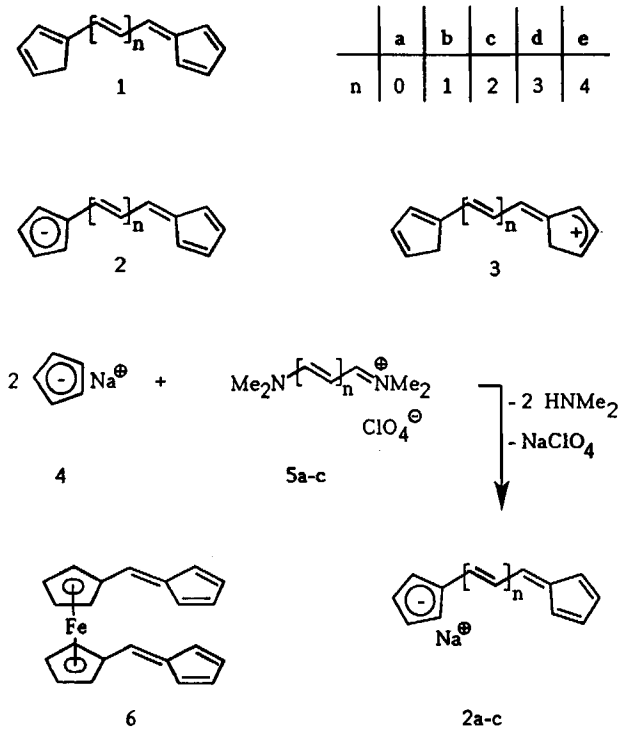
Received December 29, 1989

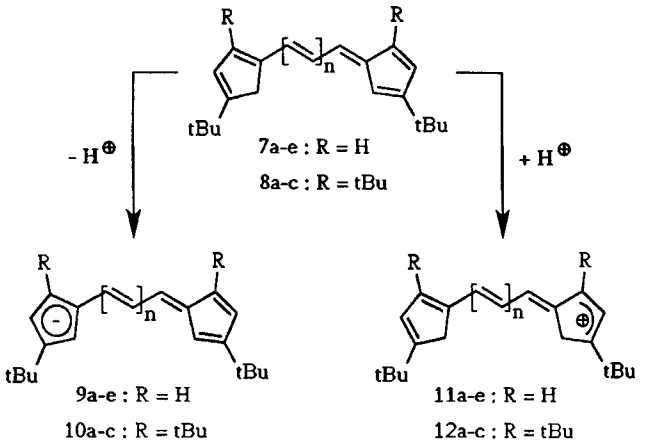
Key Words: Pentafulvene, derivatives / Alkali metal–carbanion pair structure / Cyclic voltammetry / Electrochemistry / Reversible pentafulvene protonation

The application of the principle of kinetic stabilization on vinylogous 6-(cyclopentadienyl)pentafulvenes **1** led to the synthesis of the di- and tetra-*tert*-butyl derivatives **7a–e** and **8a–c**. Their reactions with bases and acids form charged, heteroatom-free cyanine-type carbanionic **9a–e**, **10a–c** and carbocationic **11a–e**, **12a–c** species which were characterized with NMR and UV/Vis spectroscopy. Conclusions on the ion pair structures of the alkali metal salts **9a–e** and **10a–c** are drawn from the spectroscopic data. Additionally, in one case the behavior of the alkali metal salt **10b** towards oxidants was studied by cyclic voltammetry and the structure of the corresponding hydrocarbon **8b** was proved by X-ray structural analysis.

Vinylogous 6-(cyclopentadienyl)pentafulvenes **1** are suitable precursors for the preparation of the charged cyanines **2** and **3**, which consist only of carbon and hydrogen. Jutz and Amschler[1] first reported the generation of the deeply coloured sodium salts **2a–c** in solution by condensation of sodium cyclopentadienide **4** with the vinamidinium salts **5a–c**. Starting from **2a**, Müller-Westerhoff et al.[2] prepared the ferrocene **6**. All attempts to isolate the hydrocarbons **1a–c** by hydrolysis of **2a–c** failed, probably due to their extreme tendency to polymerize. Stabilization could be achieved only in the case of the corresponding indene, fluorene and azulene derivatives[1,3].

It seemed interesting to stabilize the basic structure **1** kinetically by introducing space-filling *tert*-butyl groups into the cyclopentadiene and pentafulvene rings[4]. These substituents should hardly influence the electronic properties of the π-electron system. Deprotonation of the hydrocarbons **7** and **8** should provide the carbanionic species **9** and **10** while treatment with strong acids should lead to **11** and **12**.





Synthesis and Spectroscopic Properties of Hydrocarbons 7a–e and 8a–c and Their Alkali Metal Salts 9a–e and 10a–c

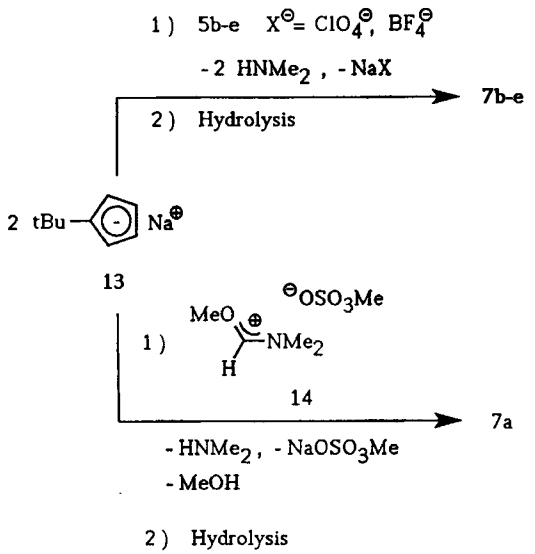
Similarly to the procedure of Jutz and Amschler[1], sodium *tert*-butylcyclopentadienide **13** reacts with **5b–e** in a 2:1 ratio to give the sodium salts **9b–e**, which form the hydrocarbons **7b–e** as mixtures of *E*/*Z* isomers after hydrolysis. **7a** can be prepared in the same way using the dimethylform-

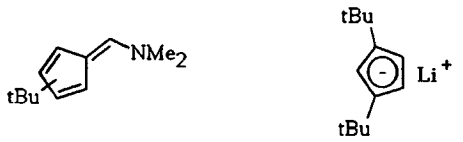
[+] Present address: Hoechst AG, Allgemeine Pharmaforschung, D-6230 Frankfurt 80, F.R.G.

  0009–2940/90/0606–1421 $ 02.50/0

amide/dimethyl sulfate adduct **14** or by adding **13** to (*E*/*Z*)-2-*tert*-butyl-6-(dimethylamino)pentafulvene (**15**)[2,5].

With an increasing number of double bonds in the bridge the stability of the products decreases, requiring gentler reaction conditions and causing a decrease in yields (Table 1). Besides **7e**, the next lower homologue **7d** is also formed, probably because the nonamethinium salt **5e** decomposes to **5d** in the presence of the dimethylamine[6] which is generated during the reaction.



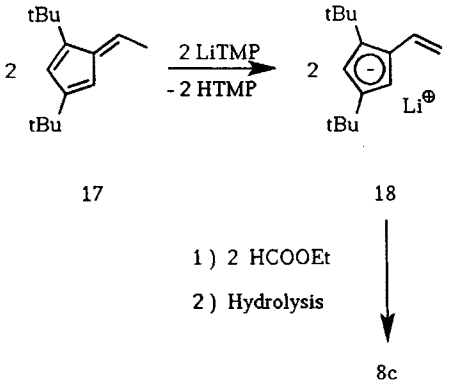


15 16

Table 1. Yields and reaction conditions for the synthesis of **7a–e** and **8a–c**

	Yield	Reaction Conditions
7a	50 %	12 h reflux (DME/diethyleneglycol dimethyl
7b	90 %	17 h reflux " ether 1:1)
7c	55 %	1 h reflux "
7d	30 %	0.5 h reflux "
7e	26 %	4 h 60°C "
8a	33 %	14 h reflux (ether)
8b	55 %	26 h reflux (THF/dichloromethane 2:1)
8c	24 %	10 h reflux (THF) *(different method)*

Just as for **7a–e**, the higher substituted 6-(cyclopentadienyl)pentafulvenes **8a** and **8b** can also be synthesized, by using lithium 1,3-di-*tert*-butylcyclopentadienide **16**. The method fails in the case of the higher homologues **8c–e** because **16** is much less reactive towards electrophiles than **13**. The pentamethine derivative **8c** may be prepared by reaction of lithium 1,4-di-*tert*-butyl-2-vinylcyclopentadienide **18** with ethyl formate. **18** is obtained by deprotonation of (*E*)-1,3-di-*tert*-butyl-6-methylpentafulvene (**17**)[7] with lithium 2,2,6,6-tetramethylpiperidide (LiTMP).



While the hydrocarbons **7a–e** must be stored under inert gas atmosphere and below 0°C, the higher substituted compounds **8a–c** are stable at room temperature and in the presence of air.

The pentafulvenes **7a–e** and **8a–c** can be quantitatively deprotonated with bases like lithium diisopropylamide or potassium *tert*-butylate to the alkali metal salts of **9a–e** and **10a–c**. The trimethine **10b** serves best as a model compound for studying the chemical properties of these species because as well as two sterically hindered five-membered rings it possesses just one atom in the bridge, bearing a partial negative charge. The crystal structure[8] of the corresponding hydrocarbon **8b** exhibits a planar π-electron system with five-membered rings shielded by the space-filling *tert*-butyl substituents, whereas the bridge shows less steric hindrance (Figure 1, Tables 2 and 3). Therefore, the reactions of **10b** with electrophiles should yield product mixtures resulting from ring and bridge attack.

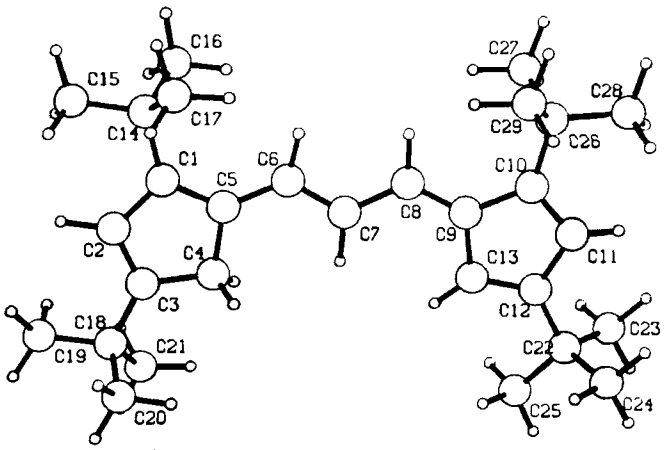
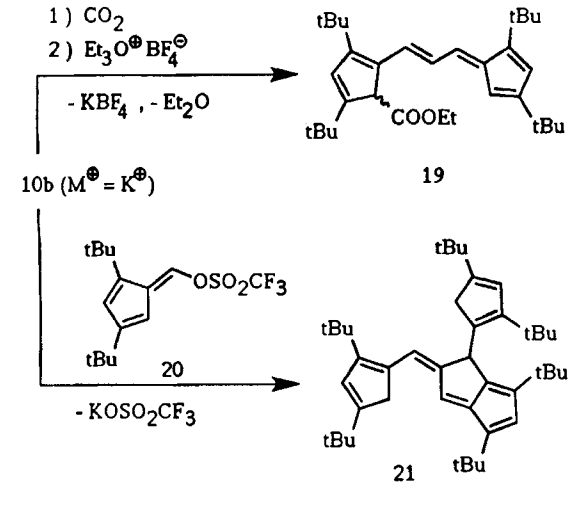


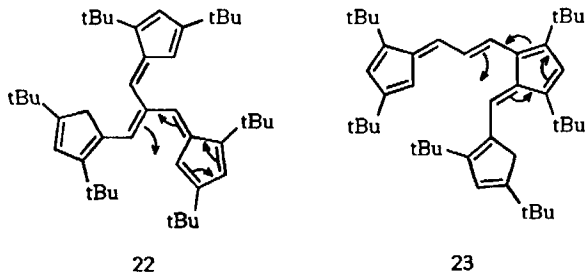
Figure 1. Crystal structure of **8b**. The numbering of the atoms is the same as in the Tables 2 and 3 and does not corresponds to nomenclature

The carboxylation of **10b**, immediately followed by reaction with triethyloxonium tetrafluoroborate, leads exclusively to the racemic ester **19** of the cyclopentadienecarbox-

Table 2. Fractional atomic coordinates and equivalent U values of **8b**. The numbering of the atoms is the same as in Figure 1 and Table 3 and does not correspond to nomenclature. Standard deviations in the least significant digit appear in parentheses

Atom	X/A	Y/B	Z/C	U_{eq}
C(1)	0.1320(03)	-0.0708(08)	0.9426(02)	0.054(02)
C(2)	0.0519(03)	0.0333(08)	0.9154(02)	0.061(02)
C(3)	0.0303(03)	0.1429(08)	0.8662(02)	0.061(03)
C(4)	0.0983(03)	0.1148(10)	0.8591(02)	0.070(03)
C(5)	0.1613(03)	-0.0266(08)	0.9093(02)	0.057(02)
C(6)	0.2363(03)	-0.0938(09)	0.9164(02)	0.063(03)
C(7)	0.2588(03)	-0.0404(09)	0.8804(02)	0.065(03)
C(8)	0.3338(03)	-0.1208(09)	0.8891(02)	0.061(02)
C(9)	0.3595(02)	-0.0819(08)	0.8540(02)	0.054(02)
C(10)	0.4337(02)	-0.1626(07)	0.8598(02)	0.048(02)
C(11)	0.4319(03)	-0.0792(08)	0.8140(02)	0.057(02)
C(12)	0.3588(03)	0.0594(07)	0.7779(02)	0.052(02)
C(13)	0.3150(03)	0.0569(08)	0.8015(02)	0.058(03)
C(14)	0.1728(03)	-0.2020(09)	0.9984(02)	0.068(03)
C(15)	0.1206(04)	-0.2072(17)	1.0219(03)	0.158(06)
C(16)	0.2559(04)	-0.0945(11)	1.0443(02)	0.093(03)
C(17)	0.1900(04)	-0.4430(10)	0.9902(03)	0.098(04)
C(18)	-0.0482(03)	0.2667(09)	0.8246(02)	0.070(03)
C(19)	-0.1007(04)	0.2941(16)	0.8475(03)	0.147(06)
C(20)	-0.1005(04)	0.1297(13)	0.7695(03)	0.104(04)
C(21)	-0.0317(04)	0.4878(12)	0.8069(03)	0.123(05)
C(22)	0.3384(03)	0.1817(08)	0.7239(02)	0.061(02)
C(23)	0.4126(03)	0.3182(09)	0.7370(02)	0.082(03)
C(24)	0.3201(03)	0.0027(09)	0.6785(02)	0.082(03)
C(25)	0.2646(03)	0.3361(11)	0.7004(02)	0.098(04)
C(26)	0.5012(03)	-0.3083(08)	0.9072(02)	0.056(02)
C(27)	0.5445(03)	-0.1840(09)	0.9647(02)	0.070(03)
C(28)	0.5671(03)	-0.3587(10)	0.8953(02)	0.080(03)
C(29)	0.4675(03)	-0.5339(09)	0.9114(02)	0.080(03)





ylic acid. Products resulting from a reaction at the bridge could not be isolated.

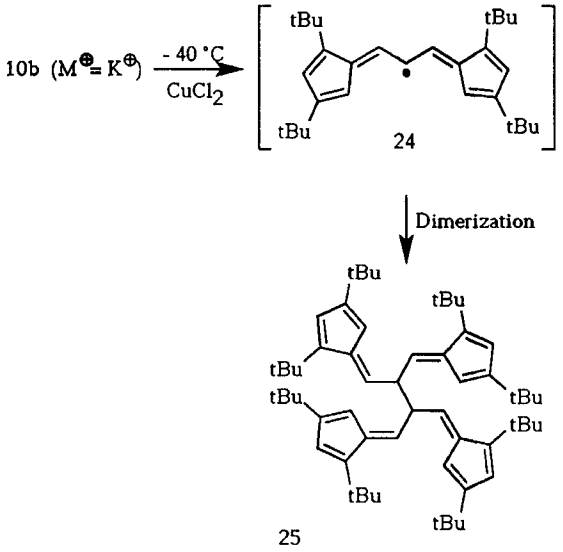
Larger electrophiles, such as pentafulvenes with a suitable leaving group at the exocyclic carbon atom, should prefer an attack at the central bridge position. Surprisingly, the reaction of **10b** with (*E*)-1,3-di-*tert*-butyl-6-(trifluoromethylsulfonyloxy)pentafulvene (**20**)[9] leads directly to the 1,2-dihydropentalene derivative **21**, which obviously results from an 8π-electrocyclic reaction of either the intermediate **22** or **23**.

Table 3. Bond lengths (Å) and angles (degree) of **8b**. The numbering of the atoms is the same as in Figure 1 and Table 2 and does not correspond to nomenclature. Standard deviations in the least significant digit appear in parentheses

C2 - C1	1.445(6)		C5 - C1 - C2	108.0(4)
C3 - C2	1.363(6)		C3 - C2 - C1	111.4(4)
C4 - C3	1.471(6)		C4 - C3 - C2	107.3(4)
C5 - C4	1.503(6)		C5 - C4 - C3	105.5(4)
C5 - C1	1.374(5)		C4 - C5 - C1	107.9(4)
C6 - C5	1.432(6)		C6 - C5 - C1	130.6(4)
C7 - C6	1.354(6)		C6 - C5 - C4	121.6(4)
C8 - C7	1.436(6)		C7 - C6 - C5	125.4(4)
C9 - C8	1.359(5)		C8 - C7 - C6	122.4(5)
C10 - C9	1.457(6)		C9 - C8 - C7	126.0(4)
C11 - C10	1.363(6)		C10 - C9 - C8	128.6(4)
C12 - C11	1.458(6)		C11 - C10 - C9	106.6(4)
C13 - C12	1.355(6)		C12 - C11 - C10	110.6(4)
C13 - C9	1.472(6)		C13 - C12 - C11	107.6(4)
			C12 - C13 - C9	108.4(4)
			C13 - C9 - C8	124.8(4)
			C13 - C9 - C10	106.7(3)
C14 - C1	1.515(6)		C15 - C14 - C1	111.9(4)
C14 - C15	1.503(6)		C16 - C14 - C1	110.4(4)
C14 - C16	1.538(7)		C16 - C14 - C15	107.8(5)
C14 - C17	1.516(7)		C17 - C14 - C1	111.0(4)
			C17 - C14 - C15	108.4(5)
			C17 - C14 - C16	107.1(5)
C18 - C3	1.502(6)		C19 - C18 - C3	111.8(4)
C18 - C19	1.505(7)		C20 - C18 - C3	109.9(5)
C18 - C20	1.523(7)		C20 - C18 - C19	105.1(5)
C18 - C21	1.501(8)		C21 - C18 - C3	111.4(5)
			C21 - C18 - C19	112.3(6)
			C21 - C18 - C20	106.0(5)
C22 - C12	1.520(6)		C23 - C22 - C12	109.6(4)
C22 - C23	1.521(6)		C24 - C22 - C12	108.0(4)
C22 - C24	1.539(6)		C24 - C22 - C23	108.1(4)
C22 - C25	1.517(6)		C25 - C22 - C12	111.8(4)
			C25 - C22 - C23	109.7(4)
			C25 - C22 - C24	109.6(4)
C26 - C10	1.514(6)		C27 - C26 - C10	110.3(4)
C26 - C27	1.529(6)		C28 - C26 - C10	110.3(4)
C26 - C28	1.541(6)		C28 - C26 - C27	106.7(4)
C26 - C29	1.525(6)		C29 - C26 - C10	111.4(4)
			C29 - C26 - C27	110.3(4)
			C29 - C26 - C28	107.6(4)

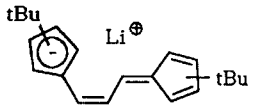
Treatment of the potassium salt **10b** with anhydrous copper chloride at −40 °C in THF exclusively gives the dimer **25** in yields of up to 80%. This regioselective reaction seems to proceed very rapidly, via the radical **24**. Even the presence of radical-trapping reagents such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl does not lead to corresponding trapping products. Cyclic voltammetry of the lithium or potassium salt of **10b** carried out in dichloromethane[10] at room temperature with a scanning rate of 0.1 − 0.5 V/s shows an ir-

reversible oxidation peak at $U = 0.9-1.0$ V (vs. H_2O/Ag/AgCl). Measurements of the potassium salt of **10b** at higher scanning velocities (150 V/s) and lower temperatures (−50°C) give no evidence for a reduction of the radical **24** (Figure 2). This interesting observation can be explained by a very high rate of the coupling reaction.



The alkali metal salts **9a−e** and **10a−c** show a characteristic colour in solution which depends on the solvent and on the cation (see experimental section). Although they possess high thermal stability, these salts are very sensitive towards air and water.

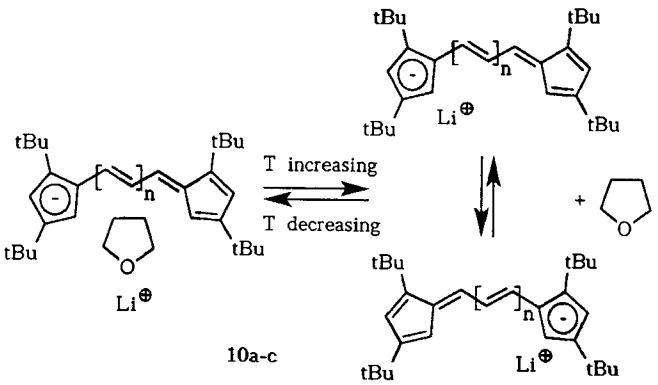
The ^{1}H-NMR spectra of the lithium salts of **9a−d** in [D_8]THF show line-broadening at temperatures below 20°C due to a restricted rotation of the bridge C−C bonds. At higher temperatures (+50°C), the signals become sharp and point to a symmetrical structure for all except the trimethine derivative **9b**. The central bridge proton in this compound is detected as a doublet of doublets instead of a triplet and the vicinal protons show two different doublets. This different behavior which also was not observed with the higher substituted lithium salts of **10a−c**, can be explained in terms of the formation of an aggregate with one bond of the bridge preferring the *cis* conformation.



9b

Different results are obtained from the ^{1}H- and ^{13}C-NMR spectra of the tetra-*tert*-butyl compounds **10a−c** (lithium salts, [D_8]THF/[D_{10}]ether, 1:1) [Figure 3 (a)]. Due to the increased steric hindrance, they show no rapid rotation even at temperatures up to +60°C so that their NMR signals remain sharp. An alteration of the chemical shifts of the hydrogen and carbon atoms is observed with decreasing temperature, which can be explained in terms of a reversible change from a contact ion pair to a solvent-separated ion pair. This entropy-controlled effect has also been observed with other organic alkali metal salts and has been examined by UV/Vis[11], ^{1}H-[12] and ^{13}C-NMR[13], ESR spectroscopy[14], and X-ray structure analysis[14].

In the contact ion pair, the π-electron density is increased in that part of the anion which is coordinated to the metal. Charge reduction in the remaining π-electron system occurs simultaneously. In fact, an increase of the temperature leads to a significant shift of the ^{13}C-NMR signal of the charged bridge carbon atoms towards lower field. The chemical shifts of the ring carbon atoms remain nearly unchanged. From this behavior, it can be concluded that the metal ion prefers coordination to a cyclopentadienide system and fluctuates rapidly between the two equivalent five-membered rings in each carbanion molecule within the NMR timescale. This intra- or intermolecular process causes an averaging effect on the chemical shifts of their ^{13}C-NMR signals so that they remain roughly constant.



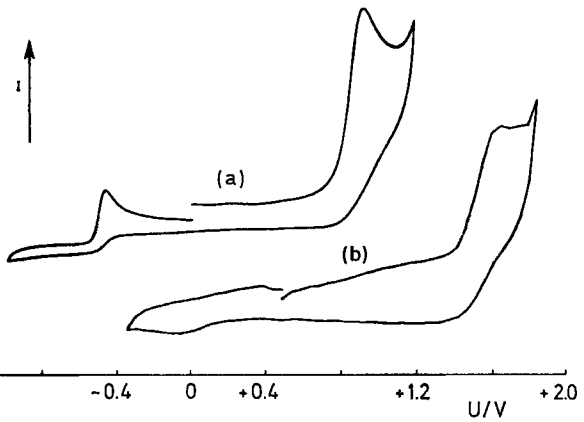


Figure 2. CV diagrams of **10b** ($M^{\oplus}$ = $K^{\oplus}$)[10]. (a) T = 298 K, vs. H_2O/Ag/AgCl, scan rate 100 mV/s. (b) T = 223 K, vs. Ag, scan rate 150 V/s. The current scales are not comparable

The lithium salt **26** offers two different cyclopentadienide systems as possible ligands so that the cation could prefer one of them. Therefore, increasing the temperature could cause a high-field shift for the signals of the carbon atoms of the coordinated ring and an inverse behavior for the others.

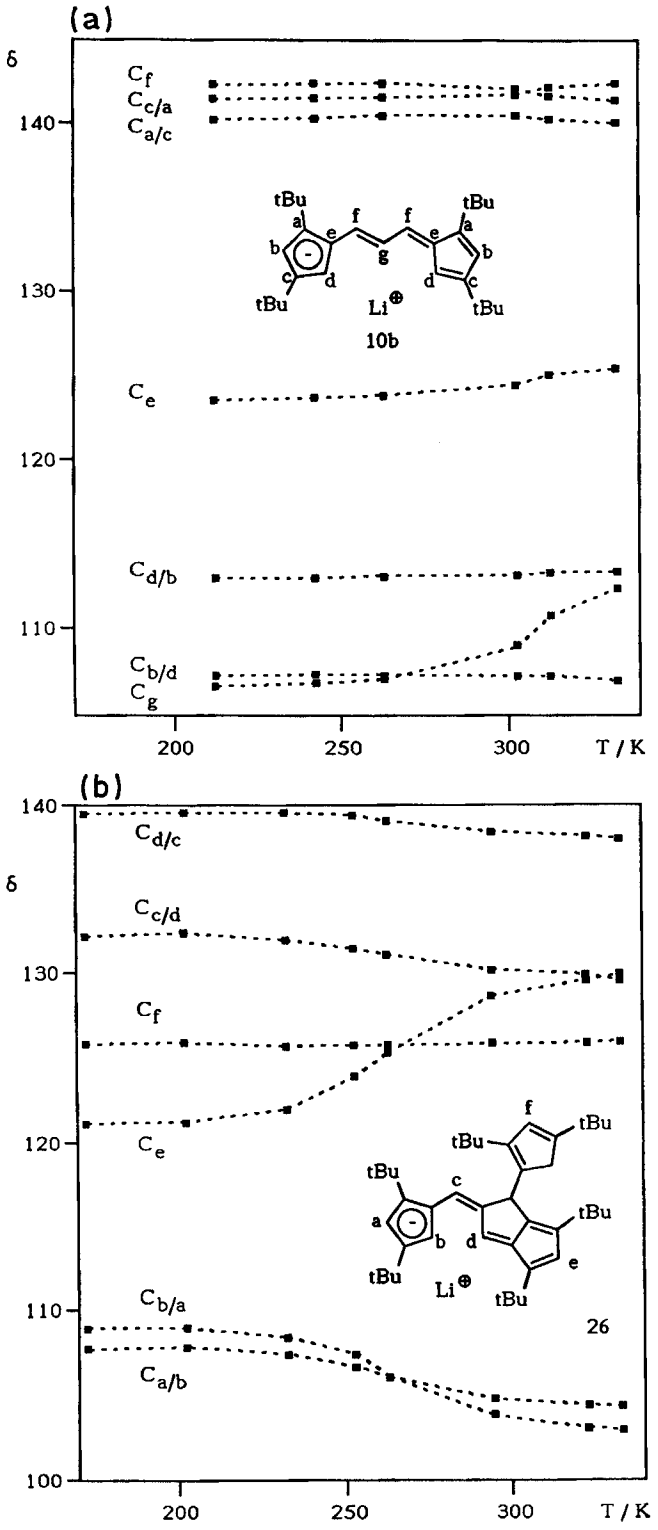
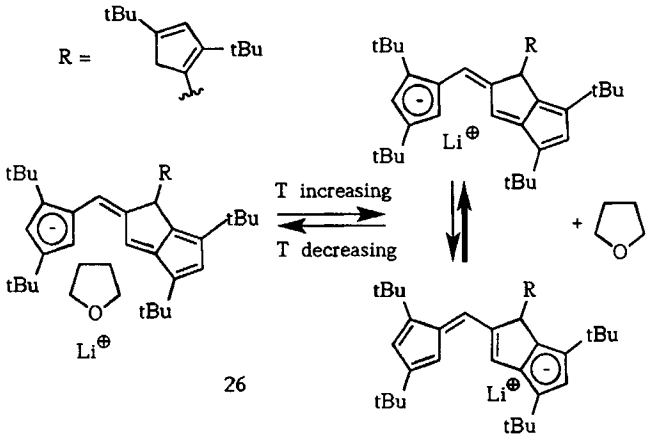


Figure 3. δ(^{13}C) of **10b** ($M^{\oplus}$ = $Li^{\oplus}$, [D_8]THF/[D_{10}]ether, 1:1) (a) and of **26** ($M^{\oplus}$ = $Li^{\oplus}$, [D_8]THF) (b)[15] as functions of temperature. The dotted lines were not measured but show the trends of the chemical shifts

The ^{13}C-NMR spectra of **26** in [D_8]THF between −100 °C and +60 °C show the expected effect for the signals of the hydrogen-substituted carbon atoms C_a–C_e[15] of the charged substructure [Figure 3 (b)]. The chemical shift of C_f in the neutral cyclopentadienyl substituent remains unchanged. The ^{1}H-NMR spectra correlate with these data; additionally, a significant change of the color of the sample from violet to blue can be observed when its temperature is decreased from 0 °C to −20 °C.



In agreement with the theoretical approach, the signals of C_a and C_b are shifted to higher field if the temperature rises, due to the increase of charge in the corresponding ring. Simultaneously, the signal due to C_e in the other ring is shifted to lower field ($\Delta\delta \approx 9$ ppm), a fact that is readily explained by a reduction of negative charge. From this, it can be concluded that in the contact ion pair, the lithium ion is favourably coordinated to the less substituted five-membered ring bearing C_a and C_b, which causes a deshielding of the remaining part of the π-electron system.

The thermodynamic parameters of the equilibrium between contact ion pair and solvent-separated ion pair can

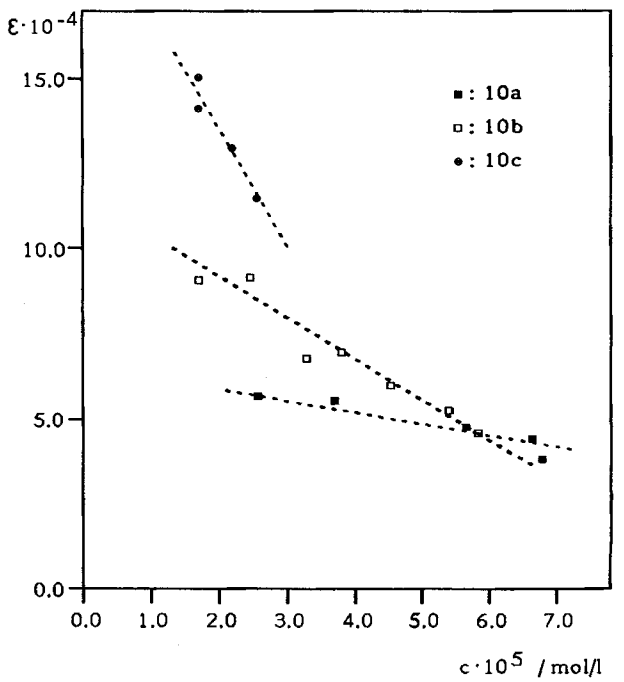


Figure 4. The extinction coefficient ε of the absorption maxima of **10a–c** ($M^{\oplus}$ = $Li^{\oplus}$, THF) as function of the carbanion concentration

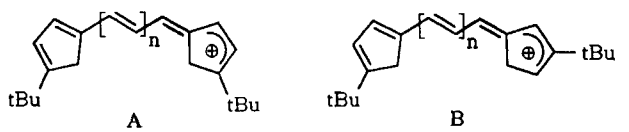
be derived from the ^{13}C-NMR spectra[13]. The spectral data of C_e were used for the calculation because its peak shows the highest sensitivity in shift towards temperature changes. Within the temperature range (−100°C to +60°C), almost complete conversion of the contact ion pair (above +50°C) into the solvent-separated ion pair (below −70°C) can be observed. This allows the determination of the *K* values with sufficient precision. The resulting values for the enthalpy and the entropy ($\Delta H = -35.5 \pm 1.5$ kJ/mol, $\Delta S = -135 \pm 7$ J/mol · K) correspond to those obtained from other systems[11-13].

Additionally, UV/Vis spectra of the oxygen-sensitive lithium salts **10a−c** where measured in THF with concentrations ranging from 17 to 68 μmol/l. The absorption maxima exhibit a strong increase of the extinction coefficient if the concentration is descreased (Figure 4). The wavelengths of the peaks remain constant for **10a** and **10c** but show a slight bathochromic shift in case of **10b**. The reason for this behavior is not clear, but dissociation effects could be responsible[16].

Synthesis and Spectroscopic Properties of the Cations 11a−e and 12a−c

The hydrocarbons **7a−e** and **8a−c** undergo reversible protonation at the pentafulvene moiety if they are treated with strong acids, such as trifluoroacetic acid. The resulting carbocations **11a−e** and **12a−c** exhibit deep colors (see experimental section) and are stable in the presence of oxygen. The ^{1}H- and ^{13}C-NMR spectra of the tetra-*tert*-butyl compounds **12a−c** are in agreement with the symmetrical structure of these compounds. The spectra of the less substituted derivatives **11a−c** are similar but two isomers are observed in ratios varying from 3−8:1.

The main isomer A is symmetrical, both *tert*-butyl groups being located at the ends of the π-electron system. The other, B, differs by the position of one alkyl substituent and for that reason shows no symmetry. This observation may be explained by the stabilizing effect of the *tert*-butyl groups. Only if the substituent is located at a charge-bearing carbon atom can it cause stabilization.



11a-e

Like the carbanions **10a−c**, the carbocations **11a−e** and **12a−c** also follow the empirical rule of Kuhn[17], with a shift of wavelength of their UV/Vis signals of 80−90 nm per double bond.

This work was kindly supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Dr.-Otto-Röhm-Gedächtnis-Stiftung*. M. E. thanks the *Stiftung Stipendienfonds des Verbandes der Deutschen Chemischen Industrie* for a scholarship. The authors are grateful to Prof. *H.-J. Lindner* and Dr. *H. Paulus, Technische Hochschule Darmstadt*, for the X-ray structural analysis, to Prof. *S. Hünig, E. Günther*, and *T. Haubenreich, Universität Würzburg*, and Prof. *K. Müllen* and *H.-J. Räder, Universität Mainz*, for the cyclovoltammetric measurements.

Experimental

All reactions were carried out under a nitrogen atmosphere if not specified otherwise. − For column chromatography, basic alumina [activity BII−III (Brockmann) ICN Woelm] and silica gel [70−230 mesh (ASTM) Merck] were used. − All solvents used in the reactions were dried and distilled according to standard procedures. − The physical data of the compounds were obtained using the following equipment. NMR: Bruker WM 300, AC 300 (^{1}H: 300 MHz, ^{13}C: 75.47 MHz). The NMR spectra were measured with TMS as internal standard except for the carbanions **9a−e**, **10a−c** and **26**, where the remaining hydrogen signals of [D_8]THF (Aldrich) were taken as standard. MS: Finnigan MAT 311-A/100 MS. IR: Beckman IR-5A, Perkin-Elmer 125. UV: Beckman DK-2A, UV-5240. The melting points were determined with a Kofler apparatus (Reichert, Vienna, Austria). − The compounds **15**[5], **17**[7], and **20**[9] were prepared according to the references.

1) *General Procedure for the Synthesis of* **7a−e**: 36.4 ml (40.0 mmol) of a 1.1 M solution of sodium *tert*-butylcyclopentadienide (**13**) in DME/diethylene glycol dimethyl ether (1:1) are heated together with 18.0 mmol of the corresponding polymethinium salt as follows:

7a:	12 h reflux,	3.59 g **14**	(preparation see below)
7b:	17 h reflux,	3.86 g **5b**	(tetrafluoroborate)
7c:	1 h reflux,	4.55 g **5c**	(perchlorate)
7d:	30 min reflux,	5.02 g **5d**	(perchlorate)
7e:	4 h 60°C,	5.49 g **5e**	(perchlorate)

The deeply coloured mixture is cooled to room temp. and hydrolyzed with 50 ml of a saturated aqueous solution of ammonium chloride. After adding 100 ml of ether and separating the phases, the organic phase is extracted twice with 100 ml of water, and the combined aqueous phases are extracted once with 50 ml of ether. The combined organic solutions are dried with magnesium sulfate, and the solvent is removed in vacuo at 30°C. After adsorptive filtration with *n*-hexane through basic alumina BII−III, the solvent is removed in vacuo at 30°C, and the residue is purified by column chromatography (6 cm diameter, 60 cm length) with *n*-hexane [**7e**: *n*-hexane/ether (20:1)] on silica gel. The resulting dark brown oil (**7b−e**) can be crystallized from *n*-hexane. The yields are as follows:

7a:	2.30 g (50%), oil,	b. p.	55°C/10^{-4} Torr[5]
7b:	4.55 g (90%), crystals,	m. p.	100−102°C
7c:	3.07 g (55%), crystals,	m. p.	101−105°C
7d:	1.80 g (30%), crystals,	m. p.	106−115°C
7e:	1.75 g (26%), crystals,	m. p.	110−120°C

In the preparation of **7e**, compound **7d** can also be isolated (0.36 g, 6%).

The adduct **14** can be prepared in situ by stirring a mixture of 1.52 g (20.0 mmol) of dimethyl sulfate and 1.46 g (20.0 mmol) of *N,N*-dimethylformamide for 2 h at 60°C and extracting the oil twice with dried ether after cooling to room temp.

(E/Z)-2-tert-Butyl-6-(3/4-tert-butylcyclopentadienyl)pentafulvene (**7a**): IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (C−H), 1575 (C=C). − UV (*n*-hexane): λ_{max} (lg ε) = 241 nm (3.892), 246 (3.852), 252 (3.645), 258 (3.281), 367 (4.486), 450 (2.631). − ^{1}H NMR ($CDCl_3$): δ = 1.16−1.25 (m, 18H, tBu), 3.38−3.50 (m, 2H, $-CH_2-$), 5.83−7.05 (m, 6H, =CH−). − MS (70 eV): *m/z* (%) = 254 (65) [M^+], 239 (63) [M − CH_3], 197 (26) [M − tBu], 57 (100) [tBu].

$C_{19}H_{26}$ (254.4) Calcd. C 89.69 H 10.31
Found C 89.53 H 10.10

(E/Z)-2-tert-Butyl-6-[(E)-2-(3/4-tert-butylcyclopentadienyl)vinyl]pentafulvene (**7b**): IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (s, C–H), 1576 (m, C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 221 nm (3.892) sh, 270 (3.926), 344 (4.152) sh, 364 (4.422) sh, 379 (4.579), 398 (4.585). – ^{1}H NMR ($CDCl_3$): δ = 1.17–1.22 (m, 18H, tBu), 3.20 (br. s, 2H, $-CH_2-$), 5.87–6.92 (m, 8H, =CH–). – MS (70 eV): *m/z* (%) = 280 (16) [M^+], 265 (15) [M – CH_3], 223 (13) [M – tBu], 57 (100) [tBu].

$C_{21}H_{28}$ (280.5) Calcd. C 89.94 H 10.06
Found C 89.88 H 10.40

(E/Z)-2-tert-Butyl-6-[(E,E)-4-(3/4-tert-butylcyclopentadienyl)-1,3-butadienyl]pentafulvene (**7c**): IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1} (s, C–H), 1550 (m, C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 258 nm (3.602) sh, 287 (3.914) sh, 295 (3.963), 383 (4.636) sh, 402 (4.803), 423 (4.777). – ^{1}H NMR ($CDCl_3$): δ = 1.16–1.21 (m, 18H, tBu), 3.14–3.16 (m, 2H, $-CH_2-$), 5.85–6.84 (m, 10H, =CH–). – MS (70 eV): *m/z* (%) = 306 (60) [M^+], 291 (32) [M – CH_3], 249 (39) [M – tBu], 57 (100) [tBu].

$C_{23}H_{30}$ (306.5) Calcd. C 90.13 H 9.87
Found C 89.98 H 10.01

(E/Z)-2-tert-Butyl-6-[(E,E,E)-6-(3/4-tert-butylcyclopentadienyl)-1,3,5-hexatrienyl]pentafulvene (**7d**): IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (s, C–H), 1550 (m, C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 248 nm (3.834), 268 (3.714) sh, 281 (3.688) sh, 305 (3.865) sh, 313 (3.898) sh, 317 (3.931), 403 (4.656) sh, 422 (4.786), 448 (4.713). – ^{1}H NMR ($CDCl_3$): δ = 1.16–1.21 (m, 18H, tBu), 3.15 (m, 2H, $-CH_2-$), 5.85–6.81 (m, 12H, =CH–). – MS (70 eV): *m/z* (%) = 332 (24) [M^+], 317 (12) [M – CH_3], 275 (15) [M – tBu], 57 (100) [tBu].

$C_{25}H_{32}$ (332.5) Calcd. C 90.30 H 9.70
Found C 89.75 H 10.11

(E/Z)-2-tert-Butyl-6-[(E,E,E,E)-8-(3/4-tert-butylcyclopentadienyl)-1,3,5,7-octatetraenyl]pentafulvene (**7e**): IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} (s, C–H), 1520 (m, C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 263 nm (3.835), 286 (3.799), 303 (3.802), 319 (3.902), 329 (3.950), 335 (3.936), 420 (4.840), 441 (4.950), 466 (4.860). – ^{1}H NMR ($CDCl_3$): δ = 1.15–1.20 (m, 18H, tBu), 3.11–3.14 (m, 2H, $-CH_2-$), 5.84 to 6.88 (m, 14H, =CH–). – MS (70 eV): *m/z* (%) = 358 (25) [M^+], 343 (4) [M – CH_3], 301 (6) [M = tBu), 57 (100) [tBu].

$C_{27}H_{34}$ (358.6) Calcd. C 90.43 H 9.57
Found C 89.41 H 9.62

2a) *Synthesis of (E)-1,3-Di-tert-butyl-6-(2,4-di-tert-butylcyclopentadienyl)pentafulvene* (**8a**): 250 ml of ether is added to 71.0 ml (0.100 mol) of a 1.44 M solution of *n*-butyllithium in *n*-hexane. To the refluxing mixture, 17.8 g (0.100 mol) of 1,3-di-*tert*-butylcyclopentadiene is added slowly. After 2 h a solution of 10.0 g (50.0 mmol) of the DMF/dimethyl sulfate adduct **14** (preparation see experiment 1) in 250 ml of dichloromethane is added and heating is continued at reflux for 14 h. The reaction mixture is hydrolysed with 200 ml of ice. The workup procedure is the same as described for experiment 1. Yield 6.10 g (33%) of **8a** as brown crystals, m.p. 120°C (from 2-propanol). – IR (KBr): $\tilde{\nu}$ = 1563 cm^{-1} (C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 243 nm (3.973), 256 (3.704) sh, 265 (3.375) sh, 384 (4.441). – ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 9H, tBu), 1.23 (s, 9H, tBu), 1.38 (s, 9H, tBu), 1.39 (s, 9H, tBu), 3.50 (br. s, 2H, 5′-H), 6.13 (d, *J* = 1.9 Hz, 1H, 2-H), 6.20 (dd, J_1 = 1.9 Hz, J_2 = 0.6 Hz, 1H, 4-H), 6.29 (t, *J* = 0.8 Hz, 1H, 3′-H), 7.76 (br. s, 1H, 6-H). – MS (70 eV): *m/z* (%) = 366 (47) [M^+], 351 (14) [M – CH_3], 309 (38) [M – tBu], 57 (100) [tBu].

$C_{27}H_{42}$ (366.6) Calcd. C 88.45 H 11.55
Found C 88.61 H 11.69

2b) *Synthesis of (E,E)-1,3-Di-tert-butyl-6-[2-(2,4-di-tert-butylcyclopentadienyl)vinyl]pentafulvene* (**8b**): To 18.7 ml (28.0 mmol) of a refluxing 1.5 M solution of *n*-butyllithium in *n*-hexane 5.00 g (28.0 mmol) of 1,3-di-*tert*-butylcyclopentadiene is added slowly. After 1 h the mixture is diluted with 60 ml of THF and a solution of 3.00 g (14.0 mmol) of the vinamidinium tetrafluoroborate **5b** in 40 ml of dichloromethane is added slowly over a period of 30 min. After 26 h of heating at reflux the mixture is cooled to room temperature, hydrolysed with 300 ml of water, and worked up as described in experiment 1. Yield 3.10 g (55%) of **8b** as brown needles, m.p. 134°C (from 2-propanol). – IR (KBr): $\tilde{\nu}$ = 1580 cm^{-1} (C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 210 nm (4.053), 278 (3.974), 396 (4.627), 414 (4.629). – ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 18H, tBu), 1.32 (s, 9H, tBu), 1.33 (s, 9H, tBu), 3.27 (br. s, 2H, 5″-H), 6.12 (d, *J* = 2.0 Hz, 1H, 4-H), 6.15 (d, *J* = 2.0 Hz, 1H, 2-H), 6.21 (s, 1H, 3″-H), 6.71 (dd, J_1 = 14.8 Hz, J_2 = 11.5 Hz, 1H, 1′-H), 7.04 (d, *J* = 11.5 Hz, 1H, 6-H), 7.17 (d, *J* = 14.8 Hz, 1H, 2′-H). – MS (70 eV): *m/z* (%) = 392 (50) [M^+], 57 (100) [tBu].

$C_{29}H_{44}$ (392.7) Calcd. C 88.71 H 11.29
Found C 88.76 H 11.29

2c) *Synthesis of (E,E,E)-1,3-Di-tert-butyl-6-[4-(2,4-di-tert-butylcyclopentadienyl)-1,3-butadienyl]pentafulvene* (**8c**): 2.80 g (19.0 mmol) of 2,2,6,6-tetramethylpiperidine is added at 0°C to 13.5 ml (20.2 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane. After 15 min at room temperature, the mixture is cooled to 0°C and a solution of 4.00 g (19.6 mmol) of (*E*)-1,3-di-*tert*-butyl-6-methylpentafulvene (**18**) in 30 ml of THF is added, and the solution is warmed up to room temperature. After 30 min, 1.45 g (19.6 mmol) of ethyl formate is added, and the reaction mixture is heated at reflux temperature for 10 h. After hydrolysis with 200 ml of water, the reaction is worked up as described in experiment 1. Yield 1.00 g (24%) of **8c** as brown crystals, m.p. 153°C (from 2-propanol). – IR (KBr): $\tilde{\nu}$ = 2941 cm^{-1} (s, C–H), 1580 (m, C=C). – UV (*n*-hexane): λ_{max} (lg ε) = 231 nm (3.999), 264 (3.648) sh, 295 (3.980) sh, 303 (4.033), 380 (4.410), 403 (4.639) sh, 419 (4.791), 445 (4.754). – ^{1}H NMR ($CDCl_3$): δ = 1.18 (s, 9H, tBu), 1.19 (s, 9H, tBu), 1.30 (s, 9H, tBu), 1.32 (s, 9H, tBu), 3.22 (br. s, 2H, 5″-H), 6.09 (br. d, *J* = 2.0 Hz, 1H, 4-H), 6.14 (d, *J* = 2.0 Hz, 1H, 2-H), 6.19 (s, 1H, 3″-H), 6.41 (dd, J_1 = 14.9 Hz, J_2 = 10.8 Hz, 1H, 3′-H), 6.67 (dd, J_1 = 14.2 Hz, J_2 = 10.9 Hz, 1H, 2′-H), 6.81 (dd, J_1 = 14.3 Hz, J_2 = 11.3 Hz, 1H, 1′-H), 7.04 (d, *J* = 11.3 Hz, 1H, 6-H), 7.05 (d, *J* = 15.1 Hz, 1H, 4′-H). – MS (70 eV): *m/z* (%) = 418 (50) [M^+], 403 (4) [M – CH_3], 361 (35) [M – tBu], 57 (100) [tBu].

$C_{31}H_{46}$ (418.7) Calcd. C 88.93 H 11.07
Found C 89.06 H 11.08

3) *Synthesis of (E,E)-1,3-Di-tert-butyl-6-[2-(2,4-di-tert-butyl-5-(ethoxycarbonyl)cyclopentadienyl)vinyl]pentafulvene* (**19**): 4.00 ml (2.40 mmol) of a 0.60 M solution of phenyllithium in ether is added to a solution of 0.78 g (2.00 mmol) of **8b** in 10 ml of THF. After 15 min, approximately 5 g of solid dry carbon dioxide is added. When the CO_2 evolution has subsided, 0.40 g (2.10 mmol) of triethyloxonium tetrafluoroborate is added and the mixture is stirred for 15 min. After hydrolysis with 10 ml of saturated aqueous NH_4Cl and separation of the phases, the organic phase is dried with magnesium sulfate and passed through a short column of basic alumina (BII–III) with ether. The solvent is removed in vacuo and the residue is chromatographed on a silica gel column (4 cm diameter, 50 cm length) with *n*-hexane/ether (9:1). The first fraction contains small amounts of **8b**. From the second fraction 0.51 g (55%) of **19** is obtained as brown crystals, m.p. 136–137°C (from *n*-hexane). – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (s, C–H), 1783 (s, C=O). – UV (*n*-hexane): λ_{max} (lg ε) = 279 nm (3.986), 374 (4.442) sh, 393 (4.609), 411 (4.603). – ^{1}H NMR ($CDCl_3$): δ = 1.19 (s, 9H, 3- or 4″-tBu), 1.20 (s, 9H, 4″-tBu or 3-tBu), 1.27 (t, *J* = 7.2 Hz, 3H, $-CH_2CH_3$),

1.32 (s, 9H, 1-tBu or 2″-tBu), 1.34 (s, 9H, 2″-tBu or 1-tBu), 4.13 (q, J = 7.2 Hz, 1H, $-CH_2CH_3$), 4.14 (q, J = 7.2 Hz, 1H, $-CH_2CH_3$), 4.32 (br. s, 1H, 5″-H), 6.08 (d, J = 1.9 Hz, 1H, 4-H), 6.14 (d, J = 1.9 Hz, 1H, 2-H), 6.32 (d, J = 0.8 Hz, 1H, 3″-H), 6.82 (dd, J_1 = 15.0 Hz, J_2 = 11.3 Hz, 1H, 1′-H), 6.97 (d, J = 11.3 Hz, 1H, 6-H), 7.06 (d, J = 15.0 Hz, 1H, 2′-H). – MS (70 eV): m/z (%) = 464 (90) [M^+], 449 (12) [M – CH_3], 407 (6) [M – tBu], 57 (100) [tBu].

$C_{32}H_{48}O_2$ (464.7) Calcd. C 82.70 H 10.41
Found C 82.52 H 10.52

4) *Synthesis of 4,6-Di-tert-butyl-1-(2,4-di-tert-butylcyclopentadienyl)-2-[(2,4-di-tert-butylcyclopentadienyl)methylene]-1H-pentalene* (**21**): 0.300 g (2.50 mmol) of potassium *tert*-butylate and approx. 50 mg of 18-crown-6 are added to 1.00 g (2.50 mmol) of **8b** in 50 ml of DME. After 15 min the solution is cooled to −30°C and a solution of 0.800 g (2.50 mmol) of **20** in 2.5 ml of DME is added dropwise. After 2 h the reaction mixture is warmed to room temp. Hydrolysis after 2 h with 20 ml of saturated aqueous NH_4Cl is followed by phase separation and extraction of the aqueous phase with 100 ml of water. The combined organic phases are dried with magnesium sulfate and the solvent is removed in vacuo. The brownish residue is chromatographed with *n*-hexane on a silica gel column (4 cm diameter, 50 cm length). The large brown fraction is taken and the solvent is removed in vacuo. The residue is flash-chromatographed on silica gel (column dimensions as above). The first brown fraction contains 100 mg (10%) of **21** as brown needles, m. p. 170–171°C (from 2-propanol). – IR (KBr): $\tilde{\nu}$ = 2980 (s, C–H). – UV (*n*-hexane): λ_{max} (lg ε) = 268 nm (3.964), 279 (3.987), 286 (3.970) sh, 407 (4.238) sh, 426 (4.352), 449 (4.286). – ^{1}H NMR ($CDCl_3$): δ = 1.02 (s, 9H, tBu), 1.11 (s, 9H, tBu), 1.20 (s, 9H, tBu), 1.21 (s, 9H, tBu), 1.31 (s, 9H, tBu), 1.35 (s, 9H, tBu), 2.42 (d, J = 22.4 Hz, 1H, 5‴-H), 2.61 (d, J = 22.8 Hz, 1H, 5‴-H), 3.27 (d, J = 22.0 Hz, 1H, 5″-H), 3.46 (d, J = 21.8 Hz, 1H, 5″-H), 4.96 (s, 1H, 1-H), 5.97 (s, 1H, 3‴-H), 6.21 (s, 1H, 3″-H), 6.35 (s, 1H, 5-H), 6.64 (s, 1H, 1′-H), 7.35 (s, 1H, 3-H). – MS (70 eV): m/z (%) = 580 (41) [M^+], 523 (75) [M – tBu], 57 (100) [tBu].

$C_{43}H_{64}$ (581.0) Calcd. C 88.90 H 11.10
Found C 88.44 H 11.09

5) *Synthesis of 1,1,2,2-Tetrakis(1,3-di-tert-butyl-6-pentafulvenyl)-ethane* (**25**): 12.0 g (11.0 mmol) of potassium *tert*-butylate is added to a soluion of 3.60 g (9.18 mmol) of **8b** in 50 ml of THF, stirred for 10 min and then cooled to −40°C. 1.50 g (11.0 mmol) of anhydrous $CuCl_2$ is added and the mixture is warmed up slowly. After 3 h, 30 ml of water and 100 ml of toluene are added. The phases are separated, the organic phase is extracted 6 times with 100 ml of water, dried with magnesium sulfate, and the solvent is removed in vacuo. The remaining solid is suspended in a small amount of *n*-hexane and filtered with suction. Yield 3.10 g (80%) of **25** as yellow powder, m. p. 200–201°C. The yield is the same if 2 equiv. of TMPO are added together with the $CuCl_2$. – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (s, C–H). – UV (*n*-hexane): λ_{max} (lg ε) = 273 nm (4.682), 381 (3.342). – ^{1}H NMR ($CDCl_3$): δ = 1.13 (s, 36H, tBu), 1.16 (s, 36H, tBu), 4.17 (br. t, J = 7.3 Hz, 2H, 1-H and 2-H), 5.99 (d, J = 1.5 Hz, 4H, 2′-H or 4′-H), 6.05 (d, J = 1.5 Hz, 4H, 4′-H or 2′-H), 6.31 (br. d, J = 9.4 Hz, 4H, 6′-H). – ^{13}C NMR ([D_{10}]toluene/$CDCl_3$ 2:1): δ = 29.35 [C(CH_3)$_3$], 32.31 [$C(CH_3)_3$], 33.15 [$C(CH_3)_3$], 49.28 (C-1, C-2), 111.52 (C-4′), 126.38 (C-2′), 135.03 (C-6′), 145.04 (C-5′), 147.98 (C-1′), 156.75 (C-3′). – MS (70 eV): m/z (%) = 782 (2) [M^+], 725 (1) [M – tBu], 391 (15) [M^{2+} or M – $CH(C_6H_3tBu_2)_2$], 57 (100) [tBu].

$C_{58}H_{86}$ (783.3) Calcd. C 88.93 H 11.07
Found C 88.82 H 11.16

6) *General Procedures for the Preparation of the Lithium Salts* **9a–e**, **10a–c**, *and* **26** *for NMR and UV/Vis Spectroscopy.* – a) *Preparation of Lithium 2,2,6,6-Tetramethylpiperidide* (LiTMP) *and Lithium Diisopropylamide* (LDA) *for NMR Spectroscopy:* 0.17 ml (0.25 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane is cooled to 0°C and 0.050 ml (0.30 mmol) of 2,2,6,6-tetramethylpiperidine is added. After stirring the mixture for 10 min at 0°C and for 10 min at room temperature the solvent is removed in vacuo and the white residue dried for 30 min at 10^{-4} Torr. After addition of 0.50 ml of [D_8]THF, the resulting 0.50 M solution of LiTMP is used immediately to avoid decomposition of the solvent. – A 0.18 M solution of LDA in [D_8]THF can be prepared in the same way using 0.36 ml (0.18 mmol) of a 0.50 M solution of *n*-butyllithium in *n*-hexane, 0.050 ml (0.35 mmol) of diisopropylamine, and 1.0 ml of [D_8]THF.

b) *Preparation of Phenyllithium* (LiPh) *for NMR Spectroscopy:* From 0.10 ml (0.20 mmol) of a 2.0 M solution of phenyllithium in benzene/ether (Aldrich) the solvent is removed in vacuo and the residue is dried for 30 min at 10^{-4} Torr. After addition of 0.25 ml of [D_8]THF and 0.25 ml of [D_{10}]ether, the resulting 0.4 M solution is used immediately to avoid decomposition of the solvent.

c) *Preparation of the Lithium Salts for NMR Spectroscopy:* The amount of hydrocarbon listed below is dried for 30 min in a 5-mm NMR tube connected by melting to a small flask equipped with a septum and a tap leading to a vacuum pump. After addition of the base [**9a–e** and **26**: 0.5 ml of LiTMP. **8a–c**: 0.5 ml of LiPh (^{1}H NMR) or 0.7 ml of LDA (^{13}C NMR)] the deeply coloured mixture (see below) is cooled to −196°C with liquid nitrogen. The NMR tube is evacuated (10^{-4} Torr) and separated from the flask by melting.

9a:	25 mg (0.10 mmol),	**7a**,	orange-brown
9b:	28 mg (0.10 mmol),	**7b**,	violet
9c:	31 mg (0.10 mmol),	**7c**,	blue
9d:	33 mg (0.10 mmol),	**7d**,	black
9e:	30 mg (0.084 mmol),	**7e**,	black
10a:	51 mg (0.14 mmol),	**8a**,	orange-brown
10b:	51 mg (0.13 mmol),	**8b**,	violet (above 60°C red)
10c:	50 mg (0.12 mmol),	**8c**,	blue (above 60°C violet)
26:	30 mg (0.050 mmol),	**21**,	violet (below −10°C blue)

d) *Preparation of LDA for UV/Vis Spectroscopy:* To 1.9 ml (1.34 mmol) of a 0.8 M solution of *n*-butyllithium in *n*-hexane at −20°C 0.20 ml (1.4 mmol) of diisopropylamine is added. After 15 min the solvent is removed at room temp. in vacuo and the white residue is dissolved in 10 ml of THF, giving a 0.11 mM solution of LDA in THF.

e) *Preparation of the Lithium Salts* **10a–c** *for UV/Vis Spectroscopy:* 0.7–1.5 mg of hydrocarbon **8a–c** is dried in a 250-ml flask at room temp. in vacuo (10^{-4} Torr) for at least 1 h. 1.0 ml (0.11 μmol) of the 0.11 mM solution of LDA in THF (as described above) is added under an argon atmosphere. After 2 min the mixture is diluted with THF until the desired concentration is obtained. 2.5 to 3.0 ml of the solution is transferred with a gas-tight syringe into a previously dried UV sample cell equipped with a septum.

Lithium 3-tert-Butyl-1-(2-tert-butyl-6-pentafulvenyl)cyclopentadienide (**9a**): ^{1}H NMR ([D_8]THF, 50°C): δ = 1.20 (s, 18H, tBu), 5.90 (dd, J_1 = 4.2 Hz, J_2 = 1.9 Hz, 2H, 5-H, 3′-H), 6.09 (br. s, 2H, 2-H, 1′-H or 4-H, 4′-H), 6.17 (br. s, 2H, 4-H, 4′-H or 2-H, 1′-H), 6.75 (s, 1H, 6′-H). – ^{13}C NMR ([D_8]THF, 50°C): δ = 32.52 [C(CH_3)$_3$], 111.74 (br., C-2, C-1′ or C-5, C-4′), 115.59 (br., C-4, C-3′), 116.77 (br., C-5, C-4′ or C-2, C-1′), 125.46 (C-1, C-5′), 139.45 (C-6′), 144.03 (br., C-3, C-2′).

Lithium 3-tert-Butyl-1-[2-(2-tert-butyl-6-pentafulvenyl)vinyl]cyclopentadienide (**9b**): ^{1}H NMR ([D$_8$]THF, 50°C): δ = 1.20 (s, 18H, tBu), 5.95 (br. s, 2H, 2-H, ring H), 5.96 (br. s, 2H, ring H), 6.05 (br. s, 2H, ring H), 6.50 (dd, J_1 = 11.3 Hz, J_2 = 14.3 Hz, 1H, 2′-H), 6.69 (d, J = 12.0 Hz, 1H, 1′-H), 6.70 (d, J = 14.0 Hz, 1H, 6″-H). – ^{13}C NMR ([D$_8$]THF, 50°C): δ = 32.34 [C(*C*H$_3$)$_3$], 109.15 (br., =CH–), 117.03 (=CH–), 127.95 (C-1, C-5″), 143.84 (C-1′, C-6″), 145.26 (C-3, C-2″).

Lithium 3-tert-Butyl-1-[4-(2-tert-butyl-6-pentafulvenyl)-1,3-butadienyl]cyclopentadienide (**9c**): ^{1}H NMR ([D$_8$]THF, 50°C): δ = 1.19 (s, 18H, tBu), 5.92 (br. s, 2H, ring H), 5.99 (br. s, 2H, ring H), 6.04 (br. s, 2H, ring H), 6.19 (t, J = 12.7 Hz, 2H, 2′-H, 4′-H), 6.61 (t, J = 12.7 Hz, 1H, 3′-H), 6.63 (d, J = 12.7 Hz, 2H, 1′-H, 6″-H). – ^{13}C NMR ([D$_8$]THF, 50°C): δ = 32.32 [C(*C*H$_3$)$_3$], 109.39 (br., =CH–), 113.31 (=CH–), 117.10 (br., =CH–), 118.53 (=CH–), 129.93 (C-1, C-5″), 140.98 (C-1′, C-6″ or C-3′), 146.59 (C-3, C-2″), 147.30 (C-3′ or C-1′, C-6″).

Lithium 3-tert-Butyl-1-[6-(2-tert-butyl-6-pentafulvenyl)-1,3,5-hexatrienyl]cyclopentadienide (**9d**): ^{1}H NMR ([D$_8$]THF, 50°C): δ = 1.19 (s, 18H, tBu), 5.85 (t, J = 12.5 Hz, 1H, 4′-H), 5.92 (br. s, 2H, ring H), 6.05 (br. s, 4H, ring H), 6.23 (t, J = 12.7 Hz, 2H, 2′-H, 6′-H), 6.55 (t, J = 12.5 Hz, 2H, 3′-H, 5′-H), 6.62 (d, J = 12.9 Hz, 2H, 1′-H, 6″-H). – ^{13}C NMR ([D$_8$]THF, 50°C): δ = 32.32 [C(*C*H$_3$)$_3$], 109.58 (=CH–), 115.56 (=CH–), 117.17 (=CH–), 117.35 (=CH–), 119.53 (=CH–), 131.63 (C-1, C-5″), 139.87 (C-1′, C-6″ or C-3′, C-5′), 144.61 (C-3′, C-5′ or C-1′, C-6″), 147.54 (C-3, C-2″).

Lithium 3-tert-Butyl-1-[6-(2-tert-butyl-6-pentafulvenyl)-1,3,5,7-octatetraenyl]cyclopentadienide (**9e**): ^{1}H NMR ([D$_8$]THF, –80°C): δ = 1.16–1.28 (m, 18H, tBu), 5.63 (br. s, 1H, ring H), 5.75 (br. t, J = 12.5 Hz, 2H, 4′-H, 6′-H or 2′-H, 8′-H), 5.89 (br. s, 1H, ring H), 6.00 (br. s, 1H, ring H), 6.05 (br. s, 1H, ring H), 6.13 (br. s, 1H, ring H), 6.18 (t, J = 12.0 Hz, 2H, 2′-H, 8′-H or 4′-H, 6′-H), 6.32 (br. s, 1H, ring H), 6.42–6.57 (m, 5H, 1′-H, 3′-H, 5′-H, 7′-H, 6″-H). – ^{13}C NMR ([D$_8$]THF, –80°C): δ = 31.55–32.13 [br., C(*C*H$_3$)$_3$], 106.96 (br., =CH–), 114.39 (br., =CH–), 115.23 (br., =CH–), 116.89 (br., =CH–), 120.23 (br., =CH–), 122.23 (br., =CH–), 122.28 (br., =CH–), 132.62 (br., C-1, C-5″), 140.12 (br., =CH–), 143.42 (br., =CH–), 144.87 (br., =CH–), 145.15 (br., =CH–), 147.15 (C-3 or C-2″), 149.50 (C-2″ or C-3).

Lithium (E)-1,4-Di-tert-butyl-2-(1,3-di-tert-butyl-6-pentafulvenyl)cyclopentadienide (**10a**):

UV (THF)

c [10^{-5} mol/l]	6.77	6.62	5.66	3.71	2.57
λ_{max} [nm]	497	497	497	497	497
lg ε	4.587	4.650	4.682	4.747	4.756

^{1}H NMR ([D$_8$]THF): δ = 1.19 (s, 18H, tBu), 1.37 (s, 18H, tBu), 5.70 (d, J = 2.2 Hz, 2H, 5-H, 2′-H), 6.38 (br. d, J = 2.2 Hz, 2H, 3-H, 4′-H), 7.81 (br. s, 1H, 6′-H). – ^{13}C NMR ([D$_8$]THF/[D$_{10}$]ether, 1:1, 30°C): δ = 110.65 (C-3, C-4′ or C-5, C-2′), 111.37 (C-5, C-2′, or C-3, C-4′), 121.65 (C-2, C-5′), 135.45 (C-6′), 141.43 (C-1, C-1′ or C-4, C-3′), 141.95 (C-4, C-3′ or C-1, C-1′).

Lithium (E)-1,4-Di-tert-butyl-2-[2-(1,3-di-tert-butyl-6-pentafulvenyl)vinyl]cyclopentadienide (**10b**):

UV (THF)

c [10^{-5}mol/l]	5.83	5.41	4.53	3.81	3.29	2.47	1.71
λ_{max} [nm]	573	574	578	580	583	583	582
lg ε	4.666	4.724	4.780	4.845	4.833	4.961	4.957

^{1}H NMR ([D$_8$]THF): δ = 1.16 (s, 18H, tBu), 1.30 (s, 18H, tBu), 5.70 (d, J = 2.3 Hz, 2H, 5-H, 2″-H), 6.08 (br. d, J = 2.3 Hz, 2H, 3-H, 4″-H), 6.41 (t, J = 12.7 Hz, 1H, 2′-H), 7.15 (d, J = 12.7 Hz, 2H, 1′-H, 6″-H). – ^{13}C NMR ([D$_8$]THF/[D$_{10}$]ether, 1:1, 30°C): δ = 107.20 (C-3, C-4″ or C-5, C-2″), 108.93 (C-2′), 113.08 (C-5, C-2″ or C-3, C-4″), 124.47 (C-2, C-5″), 140.23 (C-1, C-1″ or C-4, C-3″), 141.85 (C-4, C-3″ or C-1, C-1″), 142.07 (C-1′, C-6″).

Lithium (E)-1,4-Di-tert-butyl-2-[4-(1,3-di-tert-butyl-6-pentafulvenyl)-1,3-butadienyl]cyclopentadienide (**10c**):

UV (THF)

c [10^{-5} mol/l]	2.57	2.20	1.71	1.71
λ_{max} [nm]	678	678	678	678
lg ε	5.061	5.113	5.150	5.178

^{1}H NMR ([D$_8$]THF): δ = 1.15 (s, 18H, tBu), 1.29 (s, 18H, tBu), 5.74 (d, J = 2.2 Hz, 2H, 5-H, 2″-H), 6.02 (br. d, J = 2.2 Hz, 2H, 3-H, 4″-H), 6.08 (t, J = 12.6 Hz, 2H, 2′-H, 4′-H), 6.62 (t, J = 12.6 Hz, 1H, 3′-H), 7.05 (d, J = 12.6 Hz, 2H, 1′-H, 6″-H). – ^{13}C NMR ([D$_8$]THF/[D$_{10}$]ether, 1:1, 30°C): δ = 107.82 (C-3, C-4″ or C-5, C-2″), 111.28 (C-2′, C-4′), 114.49 (C-5, C-2″ or C-3, C-4″), 126.33 (C-2, C-5″), 139.96 (C-1′, C-6″), 141.41 (C-1, C-1″ or C-4, C-3″), 143.43 (C-4, C-3″ or C-1, C-1″), 147.34 (C-3′).

Lithium 4,6-Di-tert-butyl-1-(2,4-di-tert-butylcyclopentadienyl)-2-(1,3-di-tert-butyl-6-pentafulvenyl)-1,3a-dihydropentalen-3a-ide (**26**): ^{1}H NMR ([D$_8$]THF): δ = 1.00 (s, 9H, tBu), 1.06 (s, 9H, tBu), 1.14 (s, 9H, tBu), 1.25 (s, 9H, tBu), 1.31 (s, 9H, tBu), 1.42 (s, 9H, tBu), 2.48 (d, J = 22.7 Hz, 1H, 5′-H), 2.63 (d, J = 22.7 Hz, 1H, 5′-H), 4.81 (s, 1H, 1-H), 5.64 (d, J = 2.5 Hz, 1H, 2″-H or 4″-H), 6.03 (s, 1H, 3′-H), 6.10 (d, J = 2.5 Hz, 1H, 4″-H or 2″-H), 6.23 (s, 1H, 5-H), 6.89 (s, 1H, 3-H or 6″-H), 7.75 (s, 1H, 6″-H or 3-H). – ^{13}C NMR ([D$_8$]THF): δ = 31.12 [C(*C*H$_3$)$_3$], 31.63 [C(*C*H$_3$)$_3$], 31.85 [C(*C*H$_3$)$_3$], 32.63 [C(*C*H$_3$)$_3$], 33.22 [C(*C*H$_3$)$_3$], 33.88 [C(*C*H$_3$)$_3$], 39.90 (C-5′), 44.34 (C-1), 103.86 [C-4″(C$_a$) or C-2″(C$_b$)], 104.81 [C-2″(C$_b$) or C-4″(C$_a$)], 116.12 (quat. C), 125.89 [C-3′(C$_f$)], 128.55 [C-5(C$_e$)], 130.25 [C-3(C$_d$) or C-6′(C$_e$)], 132.59 (quat. C), 133.19 (quat. C), 133.79 (quat. C), 135.93 (quat. C), 138.44 [C-6′(C$_c$) or C-3(C$_d$)], 139.71 (quat. C), 140.31 (quat. C), 142.15 (quat. C), 145.28 (quat. C), 149.5 (quat. C), 154.89 (quat. C).

δ(^{13}C) as a function of temperature[15] ([D$_8$]THF; see also Figure 3b)

T/K	$C_{a/b}$	$C_{b/a}$	$C_{c/d}$	$C_{d/c}$	C_e	C_f
173	107.58	108.92	132.06	139.54	121.14	125.90
203	107.81	108.99	132.24	139.73	121.22	125.91
233	107.40	108.19	131.94	139.72	122.04	125.76
253	106.71	107.30	131.58	139.47	124.00	125.79
263	106.11	106.11	131.16	139.16	125.40	125.80
295	104.81	103.86	130.25	138.44	128.55	125.89
323	104.47	103.20	129.92	138.18	129.57	125.95
333	104.41	102.95	129.77	138.08	129.97	126.01

Calculation of ΔH and ΔS: The calculation is based on the ^{13}C-NMR data of C_e. The δ values at $T = 173$ K/$T = 333$ K are taken as chemical shifts of the pure solvent-separated ion pair (SSIP)/contact ion pair (CIP):

$\delta(173\ K) = \delta_{SSIP} = 121.14 \pm 0.02$

$\delta(333\ K) = \delta_{CIP} = 129.97 \pm 0.1$

The K values are calculated as $K(T) = [\delta(T) - \delta_{SSIP}]/[\delta_{CIP} - \delta(T)]$. The error of ln$K$, Δ(ln$K$), is calculated exactly for each temperature, using Δ(δ) = 0.02 ppm. The inaccuracy in determining the temperature is neglected. From the ln$K$ vs. $1/T$ plot, ΔH and $\Delta(\Delta H)$ can be derived by estimating a maximum and a minimum slope of the possible compensating straight lines, giving $\Delta H = -35.5 \pm 1.5$ kJ/mol. ΔS and $\Delta(\Delta S)$ are calculated for each temperature measured, and then the average values are taken ($\Delta S = -135 \pm 7$ J/mol · K).

T/K	ln$K$ (Δ(ln$K$))	ΔS (Δ(ΔS))/J · mol^{-1} · K^{-1}
203	−4.70 (+0.42, −0.72)	−136.0 (+13.5, −10.9)
233	−2.18 (±0.06)	−134.4 (±7.0)
253	−0.736 (±0.035)	−134.3 (±6.3)
263	−0.070 (±0.036)	−134.5 (±6.1)
295	+1.65 (±0.09)	−134.2 (±5.9)
323	+3.05 (+0.26, −0.38)	−135.4 (+7.7, −6.9)

7) *General Procedure for the Protonation of the Hydrocarbons* **7a–e** *and* **8a–c**. – a) *Preparation for NMR Spectroscopy:* 20–40 mg of the hydrocarbon **7a–e** or **8a–c** is dissolved in 0.5 ml of $CDCl_3$ in a 5-mm NMR tube. After addition of 0.1–0.2 ml of conc. trifluoroacetic acid, the tube is shaken vigorously and the spectrum is immediately measured.

b) *Preparation for UV/Vis Spectroscopy:* Approx. 1 mg of hydrocarbon **7a–e** or **8a–c** is dissolved in dichloromethane containing 2–5 vol-% of trifluoroacetic acid. The mixture is diluted with the same solvent and spectra are taken at various concentrations. By addition of water to the solution of the protonated species, the corresponding hydrocarbons can be regenerated almost quantitatively.

2-tert-Butyl-6-(3/4-tert-butylcyclopentadienyl)-1H-pentafulvenium Trifluoroacetate (**11a**): UV (CH_2Cl_2/5% CF_3COOH): λ_{max} (lg ε) = 268 nm (3.752) sh, 297 (3.744) sh, 304 (3.782), 428 (4.072) sh, 449 (4.258), 528 (3.979) sh, 551 (4.188), 695 (3.588). – ^1H NMR ($CDCl_3/CF_3COOH$, 3:1, isomer A): δ = 1.41 (s, 18H, tBu), 3.81 (s, 4H, 1-H, 5′-H), 7.13 (d, J = 2.9 Hz, 2H, 3-H, 3′-H), 8.11 (s, 1H, 6-H), 8.40 (br. s, 2H, 4-H, 2′-H). – ^{13}C NMR ($CDCl_3/CF_3COOH$, 3:1, isomer A): δ = 29.79 [C(*C*H$_3$)$_3$], 37.47 [*C*(CH$_3$)$_3$], 41.44 (C-1, C-5′), 114.54 (q, J = 285 Hz, CF_3), 134.69 (C-3, C-3′), 147.12 (C-5, C-1′), 151.35 (C-6), 162.14 (q, J = 43 Hz, $CF_3COO^{\ominus}$), 176.15 (C-4, C-2′), 200.12 (C-2, C-4′). – In the ^1H-NMR spectrum additional peaks are observed which belong to the isomer *2-tert-butyl-6-(3-tert-butyl-cyclopentadienyl)-1H-pentafulvenium trifluoroacetate* (**11a–B**) (proportional 1/8): δ = 1.30 (s, 9H, 3′-tBu), 1.41 (s, 9H, 2-tBu), 3.78 (s, 2H, 1-H), 3.88 (br. s, 2H, 5′-H), 7.24 (d, J = 3.3 Hz, 1H, 3-H), 7.59 (br. s, 1H, 4′-H), 8.20 (s, 1H, 6-H), 8.42 (br. s, 1H, 4-H), 8.60 (br. s, 1H, 2′-H).

2-tert-Butyl-6-[2-(3/4-tert-butylcyclopentadienyl)vinyl]-1H-pentafulvenium Trifluoroacetate (**11b**): UV (CH_2Cl_2/4% CF_3COOH): λ_{max} (lg ε) = 275 nm (3.622), 288 (3.638), 333 (3.938) sh, 342 (4.083), 369 (3.519), 397 (3.562), 416 (3.571), 518 (4.037) sh, 557 (4.281) sh, 592 (4.528) sh, 632 (4.877), 793 (3.661), 936 (3.013) sh. – ^1H NMR ($CDCl_3/CF_3COOH$, 3:1, isomer A): δ = 1.36 (s, 18H, tBu), 3.68 (s, 4H, 1-H, 5″-H), 6.98 (d, J = 2.7 Hz, 2H, 3-H, 3″-H), 7.24 (t, J = 13.4 Hz, 1H, 1′-H), 7.92 (d, J = 13.4 Hz, 2H, 6-H, 2′-H), 8.04 (br. s, 2H, 4-H, 2″-H). – In the ^1H-NMR spectrum additional peaks are observed which belong to the isomer *2-tert-butyl-6-[2-(3-tert-butylcyclopentadienyl)vinyl]-1H-pentafulvenium trifluoroacetate* (**11b-B**) (proportional 1/5): δ = 1.27 (s, 9H, 3″-tBu), 1.38 (s, 9H, 2-tBu), 3.60 (br. s, 2H, 1-H or 5″-H), 3.76 (br. s, 2H, 5″-H or 1-H), 7.05–7.15 (m), 7.99 (br. s), 8.24 (br. s, 1H, 2″-H).

2-tert-Butyl-6-[4-(3/4-tert-butylcyclopentadienyl)-1,3-butadienyl]-1H-pentafulvenium Trifluoroacetate (**11c**): UV(CH_2Cl_2/4% CF_3COOH): λ_{max} (lg ε) = 326 nm (3.713), 365 (3.799) sh, 377 (3.881), 447 (3.631) sh, 464 (3.676), 551 (4.190), 591 (4.243) sh, 656 (4.545) sh, 706 (4.860), 860 (3.609). – ^1H NMR ($CDCl_3/CF_3COOH$, 3:1, isomer A): δ = 1.34 (s, 18H, tBu), 3.57 (s, 4H, 1-H, 5″-H), 6.85 (d, J = 2.8 Hz, 2H, 3-H, 3″-H), 7.02 (br. t, J = 13.4 Hz, 1′-H, 3′-H), 7.72 (d, J = 13.7 Hz, 2H, 6-H, 4′-H), 7.80 (t, J = 13.8 Hz, 1H, 2′-H), 7.82 (br. s, 2H, 4-H, 2″-H). – In the ^1H-NMR spectrum additional peaks are observed which belong to the isomer *2-tert-butyl-6-[4-(3-tert-butylcyclopentadienyl)-1,3-butadienyl]-1H-pentafulvenium trifluoroacetate* (**11c-B**) (proportional 1/3): δ = 1.26 (s, 9H, 3′-tBu), 1.36 (s, 9H, 2-tBu), 3.48 (br. s, 1H, 1-H or 5″-H), 3.64 (br. s, 1H, 5″-H or 1-H), 6.70 (m), 7.01 (t, hidden), 7.11 (s), 7.79 (m), 7.86 (t, J = 13.2 Hz, 1H, 2′-H), 8.01 (br. s, 1H, 2″-H).

2-tert-Butyl-6-[6-(3/4-tert-butylcyclopentadienyl)-1,3,5-hexatrienyl]-1H-pentafulvenium Trifluoroacetate (**11d**): UV (CH_2Cl_2/3% CF_3COOH): λ_{max} (lg ε) = 290 nm (3.679), 338 (3.539) sh, 367 (3.571) sh, 397 (3.699) sh, 414 (3.732), 465 (3.655) sh, 513 (3.785), 615 (4.283) sh, 733 (4.657) sh, 793 (4.976). The peaks at λ = 600–800 nm exhibit varying extinction coefficients at different hydrocarbon concentrations [λ_{max} = 793 nm; lg ε = 4.94–4.98 (conc. of **7d**: c = 9–11 μM)], possibly due to decomposition effects. – ^1H NMR ($CDCl_3/CF_3COOH$, 3:1, isomer A): δ = 1.31 (s, 18H, tBu), 3.52 (s, 4H, 1-H, 5″-H), 6.76 (d, J = 2.2 Hz, 2H, 3-H, 3″-H), 6.92 (br. t, J = 13.2 Hz, 2H, 1′-H, 5′-H), 6.93 (t, J = 13.2 Hz, 1H, 3′-H), 7.58 (d, J = 13.2 Hz, 2H, 6-H, 6′-H), 7.57–7.69 (m, 4H, 4-H, 2′-H, 4′-H, 2″-H). – In the ^1H-NMR spectrum additional peaks are observed which belong to the isomer *2-tert-butyl-6-[6-(3-tert-butylcyclopentadienyl)-1,3,5-hexatrienyl]-1H-pentafulvenium trifluoroacetate* (**11d-B**) (proportional 1/5): δ = 3.42 (br. s, 1H, 1-H or 5″-H), 3.58 (br. s, 1H, 5″-H or 1-H), 6.79 (br. s), 7.72 (br. s), 7.82 (br. s), 8.10 (s, 1H, 2″-H).

2-tert-Butyl-6-[8-(3/4-tert-butylcyclopentadienyl)-1,3,5,7-octatetraenyl]-1H-pentafulvenium Trifluoroacetate (**11e**): ^1H NMR ($CDCl_3/CF_3COOH$, 3:1, isomer A): δ = 1.30 (s, 18H, tBu), 3.44 (s, 4H, 1-H, 5″-H), 6.62 (br. s, 2H, 3-H, 3″-H), 6.85 (br. t, J = 13.6 Hz, 4H, 1′-H, 3′-H, 5′-H, 7′-H), 7.42–7.55 (m, 7H, 4-H, 6-H, 2′-H, 4′-H, 6′-H, 8′-H, 2″-H). – In the ^1H-NMR spectrum additional peaks are observed which belong to the isomer *2-tert-butyl-6-[8-(3-tert-butylcyclopentadienyl)-1,3,5,7-octatetraenyl]-1H-pentafulvenium trifluoroacetate* (**11e-B**) (proportional 1/3): δ = 3.37 (br. s, 2H, 1-H or 5″-H), 3.50 (br. s, 2H, 5″-H or 1-H). The other protons could not be related clearly to signals.

2,4-Di-tert-butyl-6-(2,4-di-tert-butylcyclopentadienyl)-1H-pentafulvenium Trifluoroacetate (**12a**): UV (CH_2Cl_2/5% CF_3COOH): λ_{max} (lg ε) = 263 nm (3.681), 299 (4.228), 305 (4.190), 348 (3.380), 363 (3.267) sh, 375 (3.000) sh, 392 (2.438) sh, 544 (4.628) sh, 567 (4.810) sh, 576 (4.860). – ^1H NMR ($CDCl_3/CF_3COOH$, 5:2): δ = 1.30 (s, 18H, tBu), 1.50 (s, 18H, tBu), 3.70 (s, 4H, 1-H, 5′-H), 6.95 (s, 2H, 3-H, 3′-H), 8.90 (s, 1H, 6-H).

2,4-Di-tert-butyl-6-[2-(2,4-di-tert-butylcyclopentadienyl)vinyl]-1H-pentafulvenium Trifluoroacetate (**12b**): UV (CH_2Cl_2/2% CF_3COOH): λ_{max} (lg ε) = 260 nm (3.609), 294 (3.712), 343 (4.238),

405 (3.423), 409 (3.423), 421 (3.373) sh, 622 (4.729) sh, 660 (5.076). – ^{1}H NMR ($CDCl_3/CF_3COOH$, 5:2): δ = 1.30 (s, 18H, tBu), 1.50 (s, 18H, tBu), 3.68 (s, 4H, 1-H, 5″-H), 6.87 (t, *J* = 13.3 Hz, 1H, 1′-H), 6.93 (s, 2H, 3-H, 3″-H), 8.23 (d, *J* = 13.3 Hz, 2H, 6-H, 2′-H).

2,4-Di-tert-butyl-6-[4-(2,4-di-tert-butylcyclopentadienyl)-1,3-butadienyl]-1H-pentafulvenium Trifluoroacetate (**12c**): UV (CH_2Cl_2/1% CF_3COOH): λ_{max} (lg ε) = 267 nm (3.826), 304 (3.753), 379 (4.017), 463 (3.619), 697 (4.782) sh, 750 (5.217). – ^{1}H NMR ($CDCl_3$/CF_3COOH, 5:2): δ = 1.28 (s, 18H, tBu), 1.47 (s, 18H, tBu), 3.59 (s, 4H, 1-H, 5″-H), 6.80 (s, 2H, 3-H, 3″-H), 6.85 (t, *J* = 13.2 Hz, 2H, 1′-H, 3′-H), 7.70 (t, *J* = 13.2 Hz, 1H, 2′-H), 8.08 (d, *J* = 13.2 Hz, 2H, 6-H, 4′-H).

8) *X-ray Structure Analysis of* **8b**: Flat violet prisms, $C_{29}H_{44}$, M = 392.67; space group $P2_1/c$, *a* = 19.690(1) Å, *b* = 5.924(5) Å, *c* = 28.170(2) Å, β = 124.35(2)°, *V* = 2712.8 Å^3, *Z* = 4, $D_{calcd.}$ = 0.961 g/cm^3, μ = 0.26 cm^{-1} (Mo-K_α). – Measurement of a needle (size 0.072 × 0.175 × 1.4 mm) mounted parallel to *b* on a STOE-STADI4 diffractometer (Mo-K_α radiation, graphite monochromator), cell constant determination by ±ω scan of 38 reflections with 22.1° < 2θ < 29.1°; 2739 reflections with 3° < 2θ < 40° were measured ($\overline{18} \leq h \leq 1, 0 \leq k \leq 5, \overline{23} \leq l \leq 27$), 2036 symmetry-independent reflections with $|F| \geq 2\sigma(F)$. – Structure solution by direct methods (SHELX-86)[8]. Anisotropic refinement of all carbon atoms, isotropic refinement of all hydrogen atoms with common temperature factor, hydrogen atoms at C-4 (methylene group) positioned, 324 parameters, R = 0.073, R_w = 0.069 (SHELX-76)[8].

CAS Registry Numbers

(*E*)-**5b**: 52950-92-2 / (*E,E*)-**5c**: 70669-79-3 / (*E,E,E*)-**5d**: 70669-88-4 / (*all-E*)-**5e**: 125765-08-4 / (*E*)-**7a**: 125764-83-2 / (*Z*)-**7a**: 125764-84-3 / (*E,E*)-**7b**: 125764-85-4 / (*E,Z*)-**7b**: 125764-86-5 / (*E,E,E*)-**7c**: 125764-87-6 / (*E,Z,E*)-**7c**: 125764-88-7 / (*all-E*)-**7d**: 125764-89-8 / (*E,Z,E,E*)-**7d**: 125827-39-6 / (*all-E*)-**7e**: 125764-90-1 / (*E,Z,E,E,E*)-**7e**: 125827-40-9 / (*E*)-**8a**: 125764-91-2 / (*E,E*)-**8b**: 125764-92-3 / (*E,E,E*)-**8c**: 125764-93-4 / **9a**: 125764-97-8 / (*E,X*)-**9b**: 125781-16-0 / (*E,X,E*)-**9c**: 125764-98-9 / (*E,X,E,E*)-**9d**: 125764-99-0 / (*E,X,E,E,E*)-**9e**: 125765-00-6 / (*E*)-**10a**: 125765-01-7 / (*E,E*)-**10b**: 125765-02-8 / (*E,E,E*)-**10c**: 125781-17-1 / **11a**: 125765-05-1 / **11a-B**: 125765-12-0 / (*E,X*)-**11b** · $CF_3CO_2^\ominus$: 125765-14-2 / (*E,X*)-**11b-B** · $CF_3CO_2^\ominus$: 125765-16-4 / (*E,X,E*)-**11c** · $CF_3CO_2^\ominus$: 125765-18-6 / (*E,X,E*)-**11c-B** · $CF_3CO_2^\ominus$: 125765-07-3 / (*E,X,E,E*)-**11d** · $CF_3CO_2^\ominus$: 125765-20-0 / (*E,X,E,E,E*)-**11d-B** · $CF_3CO_2^\ominus$: 125765-22-2 / (*E,X,E,E,E*)-**11e** · $CF_3CO_2^\ominus$: 125765-24-4 / (*E,X,E,E,E*)-**11e-B** · $CF_3CO_2^\ominus$: 125765-26-6 / **12a** · $CF_3CO_2^\ominus$: 125765-28-8 / (*E,X*)-**12b** · $CF_3CO_2^\ominus$: 125765-30-2 / (*E,X,E*)-**12c** · $CF_3CO_2^\ominus$: 125765-32-4 / **13**: 55562-84-0 / **14**: 21511-55-7 / **17**: 125765-09-5 / (*E,E*)-**19**: 125764-94-5 / (*E*)-**20**: 125765-10-8 / (*Z*)-**21**: 125764-95-6 / **25**: 125764-96-7 / **26**: 125765-03-9 / HCO_2Et: 109-94-4 / 1,3-di-*tert*-butyl-1,3-cyclopentadiene: 73046-16-9

1) C. Jutz, H. Amschler, *Angew. Chem.* **73** (1961) 806; *Chem. Ber.* **97** (1964) 3331.
2) A. Cassens, P. Eilbracht, A. Nazzal, W. Prössdorf, U. T. Müller-Westerhoff, *J. Am. Chem. Soc.* **103** (1981) 6367.
3) R. Kuhn, H. Fischer, *Angew. Chem.* **73** (1961) 435; R. Kuhn, *ibid.* **73** (1961) 658; C. Jutz, *ibid.* **71** (1959) 380; K. Hafner, *ibid.* **70** (1958) 413, 419; K. Hafner, H. Pelster, J. Schneider, *Liebigs Ann. Chem.* **650** (1961) 62.
4) R. Riemschneider, R. Nehring, *Monatsh. Chem.* **90** (1959) 568; R. Riemschneider, A. Reisch, H. Horak, *ibid.* **91** (1960) 805; Studiengesellschaft Kohle m.b.H. (Erf. K. Hafner), D.B.P. 1110635 (1. Febr. 1962).
5) K. Hafner, G. F. Thiele, *Tetrahedron Lett.* **25** (1984) 1445; G. F. Thiele, *Diplomarbeit*, Darmstadt 1983. – For the synthesis of **15** see: O. Helmling, *Ph. D. Thesis*, Darmstadt 1983.
6) H. E. Nikolajewski, S. Dähne, B. Hirsch, E. A. Jauer, *Angew. Chem.* **78** (1966) 1063; *Angew. Chem. Int. Ed. Engl.* **5** (1966) 1044. – For the synthesis of **5c–e** see: H. E. Nikolajewski, S. Dähne, B. Hirsch, *Chem. Ber.* **100** (1967) 2616.
7) R. Brand, *Ph. D. Thesis*, Darmstadt 1983.
8) G. W. Sheldrick, SHELX-76, University of Cambridge, Cambridge, England, unpublished; SHELX-86, Universität Göttingen, Göttingen, unpublished. – Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54465, the names of the authors, and the journal citation.
9) B. Stowasser, *Ph. D. Thesis*, Darmstadt 1988; K. Hafner, *Pure Appl. Chem.* **62** (1990) 531.
10) The experimental conditions were as follows: Alkali metal salt concentration was 1 mM in a 0.1 M solution of $N(Bu)_4BF_4$ or $N(Bu)_4PF_6$ in dichloromethane. The working electrode and the counter electrode consisted of platinum, the reference electrode was $H_2O/Ag/AgCl$ or Ag in case of the measurements at temperatures below 0°C.
11) T. E. Hogen-Esch, J. Smid, *J. Am. Chem. Soc.* **88** (1966) 307, 318; S. Gronert, A. Streitwieser, Jr., *ibid.* **110** (1988) 2836.
12) J. B. Grutzner, J. M. Lawlor, L. M. Jackman, *J. Am. Chem. Soc.* **94** (1972) 2306.
13) D. H. O'Brien, C. R. Russell, A. J. Hart, *J. Am. Chem. Soc.* **98** (1976) 7427.
14) B. Becker, V. Enkelmann, K. Müllen, *Angew. Chem.* **101** (1989) 501; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 458; W. Huber, H. Unterberg, K. Müllen, *Angew. Chem.* **95** (1983) 239; *Angew. Chem. Int. Ed. Engl.* **22** (1983) 242; J. Fiedler, W. Huber, K. Müllen, *Angew. Chem.* **98**(1986) 444; *Angew. Chem. Int. Ed. Engl.* **25** (1986) 443.
15) The signals of the other carbon atoms belonging to the π-electron system could not be unambiguously identified due to their lower intensity. The numbering C_a,C_b... was chosen for clearness within the discussion and does not correspond to nomenclature.
16) M. Schlosser, *Struktur und Reaktivität polarer Organometalle*, Springer-Verlag Berlin, Heidelberg, New York 1973.
17) H. Kuhn, *Helv. Chim. Acta* **31** (1948) 1441.

[424/89]