23. ^{1}H- and ^{13}C-NMR Investigations of Heptafulvenes[1])

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^{1}H- and ^{13}C-NMR spectra of a series of 8-R^1-substituted as well as of 8,8-R^1, R^2-disubstituted heptafulvenes, varying from inversely polarized (**3l**) to unpolar (**3h**) and polar heptafulvenes with electron-withdrawing groups (**3d**, **e**, **f**), have been analyzed and compared with those of methoxytropylium salt **5a**. The results concerning ^3J (H,H) values and ^{13}C-chemical shifts are shown in *Figs. 5* and *6*. It turns out that all the NMR parameters are strongly influenced by substituents R^1, R^2, but, contrary to planar pentafulvenes, no linear correlations of the NMR parameter *vs. Hammett* substituent constants σ^+ are obtained in the series **3l** → **3d**. ^3J coupling constants $J(2,3)/J(4,5)$ and $J(3,4)$ are not much influenced by substituent changes in the series **3l** → **3h**, but are approaching in the row **3h** → **3d**. Similarly, signals of the ^{13}C-atoms undergo a moderate shift to higher frequencies in the row **3l** → **3h** but are strongly influenced by $-M$ groups, whereby the sensitivity is decreasing in the series C(7) > C(2)/C(5) > C(3)/C(4) > C(1)/C(6). These results are essentially explained by a boat conformation of inversely polarized heptafulvenes of the type **3l** and an increasing planarization of the ring on going to polar heptafulvenes of type **3d**.

1. Introduction. – During the last 20 years, all the parent compounds of triafulvenes (**1**), pentafulvenes (**2**), heptafulvenes (**3**), and nonafulvenes (**4**) have become available, and their spectra have been thoroughly analyzed. These investigations show that the parent systems are basically non-aromatic polyenes with strongly alternating bond lengths and a comparably small dipole moment[3]). While the rings of **1** [4], **2** [5], and **3** [6] are essentially planar according to MW results, the nine-membered ring of nonafulvene is strongly deviating from planarity according to UV and NMR investigations [7].

Fulvenes are very attractive for spectroscopic investigations, because substituents at the exocyclic C-atom might change π-delocalization without having strong steric implications on the ring. In fact, early experimental work and measured dipole moments of substituted fulvenes indicate that exocyclic substituents may considerably increase π delocalization so that these derivatives may occupy an intermediate position between non-aromatic and aromatic molecules [8] [9]. According to the descriptive VB notation of *Scheme 1*, there are two classes of fulvenes with respect to substituent effects: for triafulvenes **1** and heptafulvenes **3**, electron-withdrawing groups at the exocyclic C-atom should increase π delocalization in the ring as well as charge separation. On the other hand, for pentafulvenes **2** and nonafulvenes **4**, π delocalization and charge separation should be enhanced by electron-donating substituents. This classification seems to be supported by X-ray results, especially in the case of substituted triafulvenes **1** and heptafulvenes **3** (see later).

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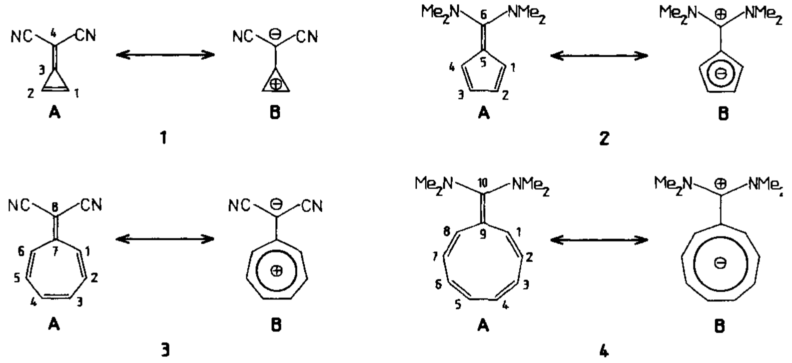
[1]) Fulvenes, Fulvalenes, Part 61; Part 60: [1].

[2]) Part of the dissertation [2].

[3]) For a recent review, see [3], spectroscopic results being summarized in Chapt. V, p. 1242.

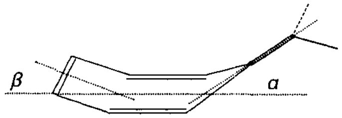
Scheme. *Substituent Effects on Fulvenes*[4])

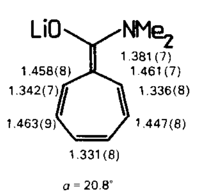
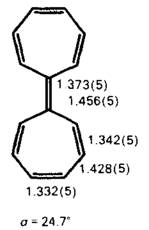
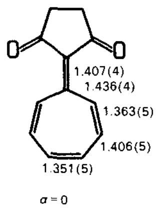
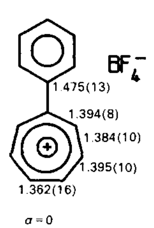


Due to the fact that most fulvenes are thermally very instable so that only rare X-ray results are available, it is desirable to investigate substituent effects by another spectroscopic method allowing measurements at low temperature. Recently, we showed for pentafulvenes **2** that substituent effects on π delocalization or bond lengths of the ring C-atoms are available from ^3J(H,H) coupling constants [11] (or from ^1J(C,C) [12]), while effects on charge density are easily derived from ^{13}C-chemical shifts: in agreement with the notation of *Scheme 1* electron-donating substituents like Me_2N groups increase π delocalization in the ring. On the other hand, the NMR-spectroscopic behavior of substituted nonafulvenes **4** is complicated by conformational effects. In most cases, the nine-membered ring of nonafulvenes strongly deviates from planarity [7].

Heptafulvenes **3** are attractive in view of a systematic NMR investigation of substituent effects on π delocalization. First of all, a considerable number of 8-substituted

Table 1. *Selected X-Ray Results of Heptafulvenes*[a])



			
α = 20.8° β = 17.9° [13][b])	α = 24.7° β = 15.7° [14]	α = 0 β = 0 [1]	α = 0 β = 0 [15]

[a]) For more structural data, see [13] and references cited therein.

[b]) Complex of two Li-heptafulvenolates · 4 THF. The second heptafulvenolate unit has very similar bond lengths, but α = 14.8° and β = 12.6°.

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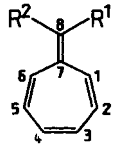
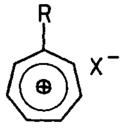
[4]) It should be mentioned that the VB notation of *Scheme 1* requires the same geometry of the two 'mesomeric forms' **A** and **B**. So, for 10,10-bis(dimethylamino)nonafulvene, there exists an *equilibrium* between the nonplanar olefinic molecule and the planarized amidinium cyclononatetraenide [10]!

and 8,8-disubstituted heptafulvenes are known [16], and during the last 15 years even a series of 'inversely polarized' heptafulvenes bearing electron-donating groups at C(8) have become available [17]. Then, the seven-membered ring of **3** bears six protons and seven C-atoms so that generally more information is available from a NMR analysis of **3** than of **1** or **2**. Finally, some X-ray data of heptafulvenes and of delocalized tropylium ions are available (*Table 1*, [2] [13–15]), so that conclusions drawn from a NMR analysis may be compared to these data. According to *Table 1*, inversely polarized heptafulvenes like **3m** or unpolar heptafulvenes like heptafulvalene assume a symmetrical boat conformation with angles α and β around 20°. Electron-accepting groups (as CO groups) at C(8) induce a planarization of the seven-membered ring. Furthermore, in agreement with the notation of *Scheme 1*, the lengths of formal single bonds and formal double bonds are approaching. However, while most formal single bonds are considerably shortened, the formal double bonds of the ring, especially C(3)=C(4), only get moderately longer on going from unpolar heptafulvenes to delocalized tropylium ions. It will be interesting to see whether these results will be confirmed by NMR spectroscopy.

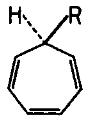
Since 1970, NMR spectra of heptafulvenes have been quite intensively investigated, although complete assignments were rare. The first complete analyses of ^{1}H-NMR spectra revealed a marked alternation of ^3J(H,H) coupling constants in 8,8-diphenylheptafulvene [18] and a medium alternation in heptafulvene-8,8-dicarbonitrile [19]. Later on, the ^{13}C-NMR spectra of the parent heptafulvene [20], and of a series of substituted heptafulvenes have been assigned [21–27]. It was found that the ^{13}C-NMR shifts of all the ring C-atoms of 8,8-diphenylheptafulvene [21] and of 8,8′-biheptafulvene [26] are very similar to those of the parent heptafulvene [20]. On the other hand, if electron-donating substituents are at C(8) of heptafulvenes or heptafulvenolates[5]), the signal of C(7) is strongly shifted to lower frequencies. This was considered as proof for an inverse polarization of this interesting class of heptafulvenes ([22–24]). However, for lithium 8-(dimethylamino)heptafulvenolate (**3m**) the free activation enthalpy for the rotation around C(7)=C(8) ($\Delta G^{\neq}$ 17.5 kcal·mol^{-1}) is very similar to that of the corresponding 3,4-dihydro derivative, which does not support a significant contribution of an anti-aromatic 8π anion to the transition state [28].



3a $R^1 = CN$, $R^2 = H$
b $R^1 = Ph$, $R^2 = H$
c $R^1 = MeO$, $R^2 = H$
d $R^1 = CF_3CO$, $R^2 = CN$
e $R^1 = R^2 = CN$
f $R^1–R^2 = CO–(CH_2)_2–CO$
g $R^1 = R^2 = Cl$
3h $R^1 = R^2 = H$
i $R^1 = R^2 = Ph$
j $R^1–R^2 = –(CH_2)_4–$
k $R^1 = NMe_3$, $R^2 = Me_3SiO$
l $R^1 = R^2 = Me_2N$
m $R^1 = Me_2N$, $R^2 = LiO$



5a $R = MeO$, $X = BF_4$
b $R = t\text{-Bu}$, $X = SbCl_6$
c $R = Ph$, $X = BF_4$



6a $R = Me_2NCO$
b $R = H$

Here, we report the results of a systematic ^{1}H- and ^{13}C-NMR investigation of a series of 8-monosubstituted (**3a–c**) and 8,8-disubstituted heptafulvenes (**3d–l**). For that purpose, some so far unknown heptafulvenes **3f**, **3g**, and **3j** have been prepared [2] and

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[5]) See *Table 1*, left formula.

analyzed [2] [29]. The NMR results will be compared to those of cycloheptatrienes **6** and of delocalized tropylium salts **5**.

2. General Remarks. – All the ^{1}H-NMR spectra of monosubstituted and unsymmetrically substituted heptafulvenes **3** were of high order even at 400 MHz. The spectra of symmetric compounds are of the type *AA'MM'XX'* and *AA'MM'XX'YY'* (**3h**). Expanded *multiplets* of the ring protons of heptafulvene-8-carbonitrile (**3a**) are shown in *Fig. 1*. The assignment is mainly based on decoupling experiments, *NOE* experiments,

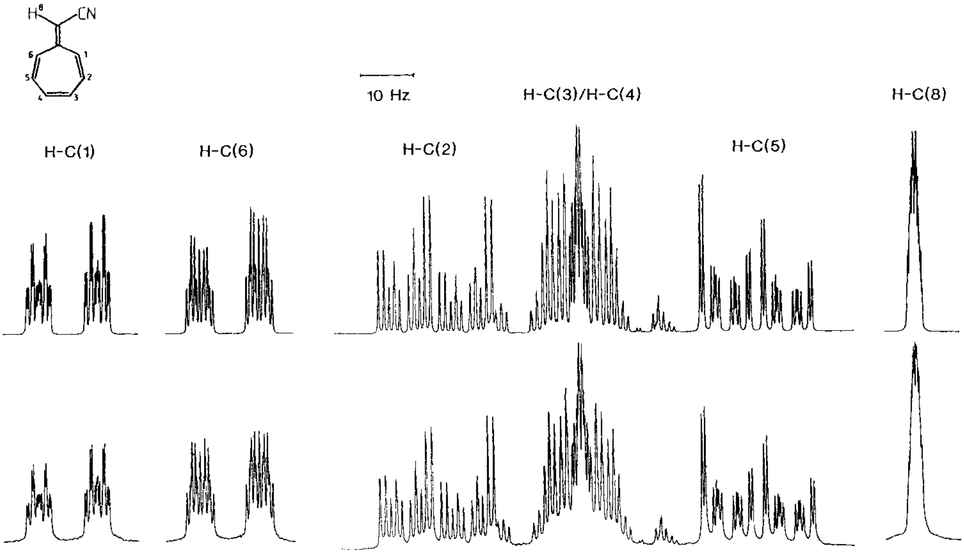

Fig. 1. *Experimental* (below) *and calculated spectrum* (above) *of heptafulvene-8-carbonitrile* (**3a**)

Table 2. *^{1}H-Chemical Shifts of Heptafulvenes* **3a–3l**, *of Tropylium Salt* **5a**, *and of Cycloheptatriene* **6a** (in (D$_6$)Acetone, ± 0.01 ppm with respect to TMS)

Compound	R^1	R^2	H–C(1)/H–C(6)	H–C(2)/H–C(5)	H–C(3)/H–C(4)	H–C(8)
3a	CN	H	6.73/6.51	6.36/6.22	6.29/6.31	4.88
3b	Ph	H	6.40/6.07	5.77/5.65	5.85/5.85	5.97
3c[a])	MeO	H	5.74/5.44	5.13/4.99	5.23/5.27	5.71
3d[b])	CF$_3$CO	CN	9.43/8.90	7.91/8.01	7.83/7.81	
3e	CN	CN	7.37	7.28	7.16	
3f[c])	CO–(CH$_2$)$_2$–CO		9.62	7.67	7.55	
3g	Cl	Cl	6.30	6.20	6.15	
3h[d])	H	H	5.97	5.48	5.65	4.43
3i	Ph	Ph	6.14	5.62	5.88	
3j[e])[f])	–(CH$_2$)$_4$–		5.82	5.51	5.70	
3k[g])	Me$_2$N	Me$_3$SiO	5.44/5.56	5.11/5.09	5.31/5.31	
3l[h])	Me$_2$N	Me$_2$N	4.84	4.37	4.71	
6a[i])			5.49	6.27	6.72	
5a[j])			8.73	9.01	8.80	

[a]) MeO: 3.57 ppm. [b]) 10°. [c]) CH$_2$: 2.52 ppm. [d]) –20°. [e]) –30°. [f]) CH$_2$: 2.08/1.65 ppm; [g]) Me$_3$SiO: 0.15 ppm; Me$_2$N: 2.53 ppm. [h]) Me$_2$N: 2.56 ppm. [i]) H–C(7): 2.46 ppm; Me$_2$N: 2.95 ppm. [j]) MeO: 4.52 ppm.

Table 3. *$^3J(H,H)$ Coupling Constants* [Hz] *of Heptafulvenes* **3** *as well as of* **5a** *and* **6a** (±0.02 Hz, 25°, (D$_6$)acetone)

Compound	R^1	R^2	$J(1,2)/J(5,6)$	$J(2,3)/J(4,5)$	$J(3,4)$
3a	CN	H	12.04/11.97	7.81/7.83	11.27
3b	Ph	H	12.06/11.86	7.32/7.11	11.41
3c	MeO	H	12.24/12.00	7.19/7.26	11.67
3d^{a})	CF_3CO	CN	11.90/11.71	8.53/8.47	10.32
3e	CN	CN	11.82	8.27	10.88
3f	CO–$(CH_2)_2$–CO		11.91	8.39	10.45
3g	Cl	Cl	11.91	7.24	11.39
3h^{b})	H	H	12.05	7.51	11.53
3i	Ph	Ph	12.13	7.21	11.28
3j^{c})	–$(CH_2)_4$–		^{d})	7.20	11.62
3k	Me_2N	Me_3SiO	11.64/11.73	6.66/6.61	11.45
3l	Me_2N	Me_2N	12.03	6.92	11.63
6a			9.34	5.96	11.63
5a			11.40	9.19	9.93

^{a}) 10°. ^{b}) –20°. ^{c}) –30°. ^{d}) Not determined due to long-range couplings of H–C(1)/H–C(6) and H–C(2)/H–C(5) with the cyclopentylidene protons.

Table 4. *Long-Range Coupling Constants* [Hz] *of Heptafulvenes* **3a**–**3l** *as well as of* **5a** *and of* **6a** (±0.02 Hz, 25°, (D$_6$)acetone)

Compound	R^1	R^2	$J(1,3)/J(4,6)$	$J(2,4)/J(3,5)$	$J(1,6)$	$J(1,4)/J(3,6)$	$J(2,5)$	$J(1,5)/J(2,6)$
3a	CN	H	0.86/0.89	1.08/1.07	2.60	0.92/0.92	–0.06	–0.15/0.10
3b	Ph	H	0.80/0.94	0.76/1.20	2.30	0.96/0.93	0.02	–0.01/0.11
3c	MeO	H	0.85/0.84	0.93/0.93	2.15	0.96/0.90	–0.01	–/–
3d^{a})	CF_3CO	CN	0.68/0.64	1.41/1.41	2.77	0.78/0.81	0.02	–0.08/–0.02
3e	CN	CN	0.90	1.19	2.82	0.79	–0.03	–0.14
3f	CO–$(CH_2)_2$–CO		1.01	1.31	2.51	0.68	0.03	–0.16
3g	Cl	Cl	0.86	1.00	2.38	0.88	0.09	–0.26
3h^{b})	H	H	0.91	0.93	2.40	0.93	–0.02	–0.18
3i	Ph	Ph	0.85	0.98	2.38	0.88	0.02	–0.24
3j^{c})	–$(CH_2)_4$–		0.84	0.89	^{d})	0.83	^{d})	^{d})
3k	Me_2N	Me_3SiO	0.70/0.77	0.79/0.91	1.80	0.98/0.93	0.02	–0.15/–0.22
3l	Me_2N	Me_2N	0.95	0.86	2.21	0.77	0.04	–0.30
6a			0.78	0.32	1.60	0.78	–	–0.53
5a			0.62	1.30	3.44	0.57	0.02	–0.08

^{a}) 10°. ^{b}) –20°. ^{c}) –30°. ^{d}) Not determined due to long-range couplings of H–C(1)/H–C(6) and H–C(2)/H–C(5) with the cyclopentylidene protons.

Table 5. *Long-Range Coupling Constants* [Hz] *between H–C(8)*^{a}) *and Ring Protons of Heptafulvenes* (±0.02 Hz, (D$_6$)Acetone)

Compound	$J(1,8)$	$J(2,8)$	$J(3,8)$	$J(4,8)$	$J(5,8)$	$J(6,8)$
3a	0.34	1.13	0.17	0.15	0.62	0.64
3b	1.02	1.33	–	–0.02	0.63	0.94
3c	0.97	1.40	–	–	0.46	0.78
3h	0.48	1.08	–	0.02	0.75	0.52

^{a}) R^2 = H–C(8), see formula; for **3h**, couplings of H′–C(8) are identical to those of H–C(8).

and spectra simulations [29]. Sets of ^{1}H-chemical shifts and of coupling constants for **3** in (D_6)acetone, obtained by computer simulation and iteration [29] using the program *PANIC* [30] are listed in *Tables 2,3,4*, and *5*.

Solvent effects on ^{1}H-chemical shifts were checked for **3i** and **3f** and found to be small: for **3i**, the differences from $CDCl_3$ to (D_6)acetone are smaller than 0.15 ppm, and for **3f**, the shifts are within 0.05 ppm for H–C(1)/H–C(6) in (D_8)THF, CD_2Cl_2, (D_6)acetone, and (D_6)DMSO. Also coupling constants are hardly affected by changes of solvents: for **3i**, the differences of ^3J values between $CDCl_3$ and (D_6)acetone are smaller than 0.05 Hz.

Temperature dependence of spectra of **3f** was determined between 80° and −95°. Protons H–C(1) and H–C(6) show the strongest effect with a low-field shift of 0.27 ppm from 80° to −95°. These effects are small compared to polar nonafulvenes [7], where both a pronounced solvent and temperature dependence is observed. All monosubstituted and nonsymmetrically disubstituted compounds produce nonsymmetric ^{1}H-NMR spectra and show no coalescence of ring protons up to room temperature. So, the double-bond

Table 6. *^{13}C-Chemical Shifts of Heptafulvenes* **3a–3l** *as well as of* **5a** *and of* **6a** ($CDCl_3$, ± 0.01 ppm with respect to TMS)

Compound	R^1	R^2	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
3a	CN	H	134.08	133.02	132.99	133.54	132.37	136.64	156.72	87.22
3b	Ph	H	132.61	128.78	131.80[a]	131.49[a]	127.05	139.70	139.1[a]	125.83
3c[b]	MeO	H	130.53	126.38	129.82	131.71	124.55	136.45	122.51	144.75
3d	CF_3CO	CN	137.73	142.84	141.58	140.46	142.65	139.89	165.20	88.19
3e	CN	CN	135.30	138.65	137.42	137.42	138.65	135.30	163.70	70.10
3f	CO–$(CH_2)_2$–CO		139.02	142.93	140.60	140.60	142.93	139.02	158.94	114.52
3g[b][c]	Cl	Cl	130.62	130.15	132.35	132.35	130.15	130.62	135.54	113.15
3h[d]	H	H	138.30	126.90	130.80	130.80	126.90	138.30	146.60	111.90
3i	Ph	Ph	135.71	127.48	132.00	132.00	127.48	135.71	136.61	135.62
3j[b][e]	$-(CH_2)_4-$		135.86	125.36	131.00	131.00	125.36	135.86	129.67	139.73
3k	Me_2N	Me_3SiO	134.30	122.82	130.61	131.61	123.63	134.30	107.48	148.76
3l	Me_2N	Me_2N	139.30	120.80	130.80	130.80	120.80	139.30	105.70	157.50
6a			118.40	124.04	129.99	129.99	124.04	118.40	41.57	170.98
5a[a]			138.92	151.73	148.01	148.01	151.73	138.92	182.17	–

[a] Assignment ambiguous. [b] (D_6)Acetone. [c] −20°. [d] From [30]. [e] −30°.

Table 7. *$^1J(^{13}C,^{13}C)$ Coupling Constants of Heptafulvenes* **3**, *of Tropylium Ion* **5a**, *and of Cycloheptatriene* **6a** (±0.3 Hz, 25°, $CDCl_3$)[a]

Compound	R^1	R^2	J(1,2)/J(5,6)	J(2,3)/J(4,5)	J(1,7)/J(6,7)	J(7,8)
5a[b]			58.9	52.3	60.9	–
3d	CF_3CO	CN	61.5/62.0	[c]	50.0/51.0	67.5
3e	CN	CN	65.2	53.2	53.2	[d]
3i	Ph	Ph	68.1	53.8	52.8	[d]
3k	Me_2N	Me_3SiO	69.4/69.4	54.1/54.1	55.2/55.0	[d]
6a			67.0	54.0	38.8	54.0

[a] J(3,4) could not be determined due to the equivalence of C(3) and C(4) for symmetric compounds or a strong *AB* effect for nonsymmetric compounds. [b] (D_6)Acetone. [c] Not determined due to a strong *AB* effect. [d] Not determined due to intensity problems.

character of the exocyclic double bond of heptafulvenes seems to be higher than for polar pentafulvenes, where often coalescence is observed [11].

^{13}C-NMR chemical shifts (*Table 6*) were assigned by $^{13}C,^{1}H$ shift-correlated spectra, as well as by off-resonance experiments. $^{1}J(^{13}C,^{13}C)$ values (*Table 7*) were determined either from the satellites of ^{1}H-decoupled ^{13}C-NMR spectra (where sensitivity is better) or by INADEQUATE experiments [31]. $^{1}J(C(3),C(4))$ values could not be determined, either due to the equivalence of the C-atoms of symmetric compounds, or because of a strong *AB* effect in the case of nonsymmetric compounds.

Due to the lack of X-ray data, *Hammet* σ^+ substituent constants [32][6]) were used for quantification of electronic substituent effects. For planar pentafulvenes with reduced steric effects, good linear correlations between σ^+ and vicinal H,H-coupling constants (showing a linear dependence on C,C bond length in the absence of other effects) or ^{13}C-chemical shifts of the ring C-atoms (showing charge density effects in the absence of steric effects) are observed [11].

3. Substituent Effects on ^{1}H-Chemical Shifts (see *Table 2*). – It is well-known that ^{1}H-chemical shifts of olefinic protons of conjugated ring systems are influenced by several factors including charge-density, anisotropy, ring-current and *van-der-Waals* effects. Electron withdrawing groups at C(8) of heptafulvenes are expected to reduce the electron density of the ring and to induce a shift of the signals of the ring protons to higher frequencies. Furthermore, they are favoring dipolar form **3B**, so that the induced ring-current effect should support this low-field shift[7]). This means that the overall 'electronic substituent effect' is expected to be large for dipolar heptafulvenes of the type **3d**, **3e**, and **3f**. Steric effects will be operative as soon as conformational changes are effective which are possible according to X-ray results (see *Table 1*), while anisotropy effects will predominantly influence the chemical shifts of H–C(1) and H–C(6).

According to *Table 2*, ^{1}H-chemical shifts of heptafulvenes are in a narrow range in most cases, but they are strongly influenced by exocyclic substituents. While electron-donating groups like Me_2N induce a high-field shift which is most pronounced for H–C(2)/H–C(5), electron-withdrawing substituents induce a low-field shift of the ring-protons. However, no linear correlations of δ values with *Hammett* σ^+ constants are observed (*Fig. 2*). It is interesting to see that the sensitivity of chemical shifts towards substituents increases in the range of electron-withdrawing groups: on going from **3l** to **3h** ($\Delta\sigma^+ = 3.34$) and then from **3h** to **3f** ($\Delta\sigma^+ = 1.04$), the $\Delta\delta$ values are 1.11 and 2.19 ppm for H–C(2)/H–C(5) or 0.94 and 1.90 ppm for H–C(3)/H–C(4), respectively. This at first sight surprising behavior is explained by a combined influence of charge-density and ring-current effect: we assume that the chemical shifts are strongly influenced by the charge-density effect, which follows from ^{13}C-NMR data (see later). With increasing

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[6]) The following literature data of *Hammett* substituent constants σ^+ have been used for the various substituents R^1, R^2 of **3** [32]: CN: +0.66; MeCO: +0.52; Cl: +0.11; Ph: –0.18; Me: –0.31; MeO: –0.78; Me_2N: –1.67; O^-: –2.30. It turns out that for CO groups at C(8) of heptafulvenes, a σ^+ of 0.78 gives a perfect fit of the NMR data of heptafulvenes **3d** and **3f**. This value is only used in *Figs. 5* and *6* (see *Discussion*). All the σ^+ values are σ_p^+ values [32].

[7]) In a clear contrast to heptafulvenes **3**, charge-density and ring-current effects are nearly counterbalancing each other in dipolar pentafulvenes **2** (like 6-(dimethylamino)pentafulvene) so that substituent effects on ^{1}H-NMR shifts are small for pentafulvenes [11]!

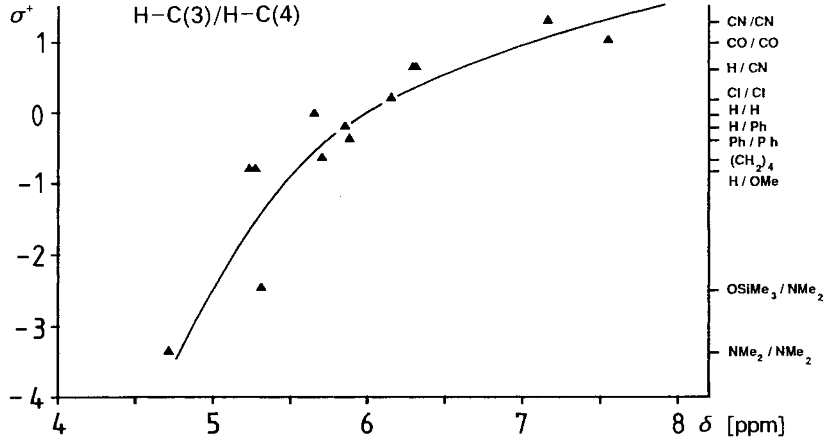

Fig. 2. *Plot of* Hammett *substituent constants* σ^+ vs. *^{1}H-chemical shifts of H–C(3)/H–C(4) of heptafulvenes*[8])

electron-withdrawing power of the substituents R^1, R^2 of **3**, the ring-current effect gets more and more operative due to planarization of the seven-membered ring (see *Table 1*) and increasing π delocalization. Since both effects are additive, a strong influence of powerful $-M$ substituents on δ values may be expected[8]) (*Fig. 2*).

Protons H–C(1)/H–C(6) are further influenced by the anisotropy effect which is most pronounced for planar **3f** (9.62 ppm), where these protons as well as the C=O groups are close to each other (according to X-ray data, the H–O distance is 2.07 Å). It may be assumed that steric effects are operative as well, especially for H–C(1)/H–C(6) in the case of planarized polar molecules, but they are dominated by other strong influences discussed above.

Finally, it is interesting to note that, in monosubstituted heptafulvenes, similar electronic effects are operative on both ring sides. For nonpolar heptafulvenes, the normal δ sequence is H–C(1)/H–C(6) > H–C(3)/H–C(4) > H–C(2)/H–C(5). Since the protons H–C(2)/H–C(5) are especially sensitive to charge-density effects according to HMO calculations, the δ sequence changes to H–C(1)/H–C(6) > H–C(2)/H–C(5) > H–C(3)/H–C(4) for heptafulvenes bearing strong electron-withdrawing groups.

4. Substituent Effects on Vicinal H,H-Coupling Constants (see *Table 3*). – Vicinal H,H-coupling constants are strongly influenced by four parameters: *a*) the dihedral angle φ, *b*) the H–C–C bond angle θ, *c*) the electronegativity of substituents, *d*) the bond length r(C,C) [33]. For planar pentafulvenes, where electron-donating substituents mainly reduce the alternation of bond lengths with increasing π delocalization, linear correlations with *Hammett* σ^+ constants are observed [11]. Exocyclic substituents of heptafulvenes additionally induce a conformational change according to X-ray results (*Table 1*): inversely polarized heptafulvenes like **3m** exist in a pronounced boat conformation, while electron-withdrawing groups induce a flattening of the ring. Contrary to pentafulvenes, vicinal H,H-coupling constants of heptafulvenes are, therefore, expected

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[8]) For unsymmetrically substituted heptafulvenes, both values are entered.

to be not only influenced by the changes of bond lengths, but by the concurrent changes of dihedral angles and, to a minor extent, of bond angles.

According to *Table 3* and *Fig. 3*, exocyclic substituents influence ^3J couplings over formal single bonds differently from ^3J couplings over formal double bonds: with increasing electron-withdrawing power of the substituents, $J(2,3)$ and $J(4,5)$ show a pronounced increase from 6.65 Hz (**3k**) to 8.50 Hz (**3d**), and the same trend is observed on going to the even more delocalized methoxytropylium cation **5a** (9.19 Hz). Furthermore, plots of σ^+ *vs.* ^3J values show no linear correlation over the whole σ^+ range, because the sensitivity of the coupling constants towards substituent changes is relatively small in the row **3l** ($R^1{=}R^2{=}Me_2N$) → **3h** ($R^1{=}R^2{=}H$), and is obviously enhanced in the presence of strong electron-withdrawing groups[9]). The changes of $J(2,3)$ and $J(4,5)$ in the series **3l** → **3d** may be related to two essential effects, namely to a ring flattening, which influences the dihedral angles of the H–C(2)=C(3)–H and H–C(4)–C(5)–H as well as to a shortening of bond lengths. Both effects occur as confirmed by X-ray and microwave data (*Table 1*).

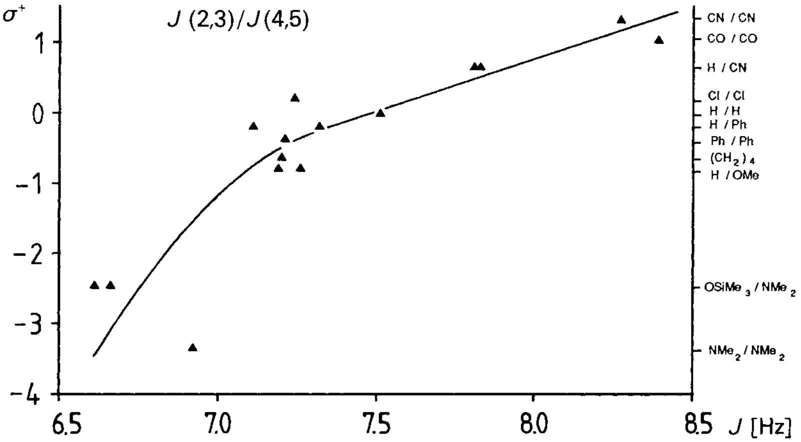

Fig. 3. *Plot of* σ^+ vs. *vicinal H,H-coupling constants J(2,3)/J(4,5) of heptafulvenes*[8])[9])

To a minor extent, changes of H–C–C bond angles from 118° in a boat conformation to 115.7° in a planar ring may slightly increase the vicinal coupling as well. Since inversely polarized heptafulvenes and non-polar heptafulvenes show very similar bond lengths, according to X-ray data, we assume that, for these compounds, the dihedral angle effect dominates.

^3J Couplings over formal double bonds show a different behavior from those over formal single bonds. As *Table 3* shows, $J(3,4)$ value moderately decreases from 11.6 (**3l**) to 10.3 (**3d**) and to 9.2 Hz (**5a**). Obviously, substituent effects are smaller; there is no linear correlation with σ^+ over the whole range[9]) and, if plotted *vs.* σ^+, there is more scattering for $J(3,4)$ than for $J(2,3)$ (*Fig. 3*). The very small changes of $J(1,2)/J(5,6)$ from 12.0 (**3l**) to 11.8 (**3d**) and 11.4 Hz (**5a**) are even more surprising and at first sight unexpected in terms of the assumed π delocalization.

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[9]) A linear correlation of σ^+ *vs.* the NMR parameter is suggested for positive σ^+ constants from modified plots with an extended σ^+ scale using slightly modified σ^+ constants for CO groups (see *Discussion* and *Figs. 5* or *6*).

^3J Couplings over formal double bonds are not expected to be influenced by changes of dihedral angles, since φ of all the segments should be close to zero according to MNDO calculations [34]. However, at least two effects with opposite influences on ^3J values are anticipated: extensive π delocalization should result in an increase of C=C bond lengths and induce a reduction of the corresponding ^3J values. On the other hand, ring planarization is expected to slightly increase H–C–C bonds angles and ^3J values as well.

Finally, substituents of monosubstituted and nonsymmetric heptafulvenes are obviously affecting both ring moieties equally. This follows from the very similar pairs of ^3J coupling constants of compounds **3a**, **3b**, **3c**, **3d**, and **3k**. The result is in agreement with both a symmetrical boat or planar-ring conformation. Furthermore, substituent effects seem to be additive, as differently disubstituted compounds with the same $\Sigma\sigma^+$ have similar coupling constants.

Summarizing, the transition from inversely polarized (**3l**) to unpolar (**3h**), to strongly polarized heptafulvenes (**3d**) and to tropylium salts (**5a**) induces an approach of the vicinal H,H-coupling constants $J(2,3)/J(4,5)$ and $J(3,4)$. While ^3J values alternate strongly for heptafulvenes of type **3l** (12.03; 6.92; 11.63 Hz), the alternation is reduced for polar heptafulvenes of type **3d** (11.8; 8.5; 10.3 Hz) and nearly disappears for tropylium salts **5**. This is certainly a result of increasing ring flattening and π delocalization, accompanied by an approach of bond lengths. In agreement with X-ray results, $J(3,4)$ and $J(4,5)$ increase somewhat more than the coupling constants over formal double bonds are reduced. The main reason is that they are influenced by two additive effects while $J(1,2)$, $J(3,4)$, and $J(5,6)$ depend on two opposite effects. The question remains, however, why in the series **3l** → **5c** bond lengths are equalizing more at the expense of a decrease of formal single bonds by 0.063 Å, while formal double bonds of the ring are only stretched by 0.040 Å (*Table 1*).

5. Substituent Effects on Long-Range Coupling Constants (see *Tables 4* and *5*). – Of all the allylic coupling constants, $^4J(1,6)$ is surprisingly large with values between 1.80 Hz (**3k**) and 3.44 Hz (**5a**). The systematic increase in the series **3k** → **5a** can be explained by ring planarization as well as by a decrease of the overall bond length of the segment C(6)–C(7)–C(1). All other ^4J coupling constants are smaller and less affected by substituents. $J(1,3)/J(4,6)$ and $J(2,4)/J(3,5)$ are of similar size (*ca.* 0.9 Hz) for non-polar or inversely polarized fulvenes. For strong electron-withdrawing groups, a moderate increase of $J(2,4)/J(3,5)$ from 0.76 Hz (**3b**) to 1.41 Hz (**3d**) is observed, while $J(1,3)/J(4,6)$ remains almost constant. The signs of all ^4J couplings are positive, as the σ mechanism dominates.

$J(1,4)/J(3,6)$ is by far the largest ^5J coupling, as two formal π bonds are involved; it is nearly unaffected by substituents. All other $^5J_{tct}$, where two σ bonds are in the C-chain, are considerably smaller.

As can be seen from *Table 5*, from all couplings of the ring protons with H–C(8), $J(2,8)$ is dominating with values between 1.08 Hz (**3h**) and 1.33 Hz (**3b**) due to the favorable arrangement of the H–C–C–C–H segment ($^5J_{ttt}$). This coupling can, therefore, be used as key argument for the assignment of H–C(2), analogous to $^5J(2,6)$ in pentafulvenes [35] [11].

6. Substituent Effects on ^{13}C-Chemical Shifts (see *Table 6*). – ^{13}C-NMR chemical shifts are mainly influenced by hybridization, charge-density effects, and steric effects;

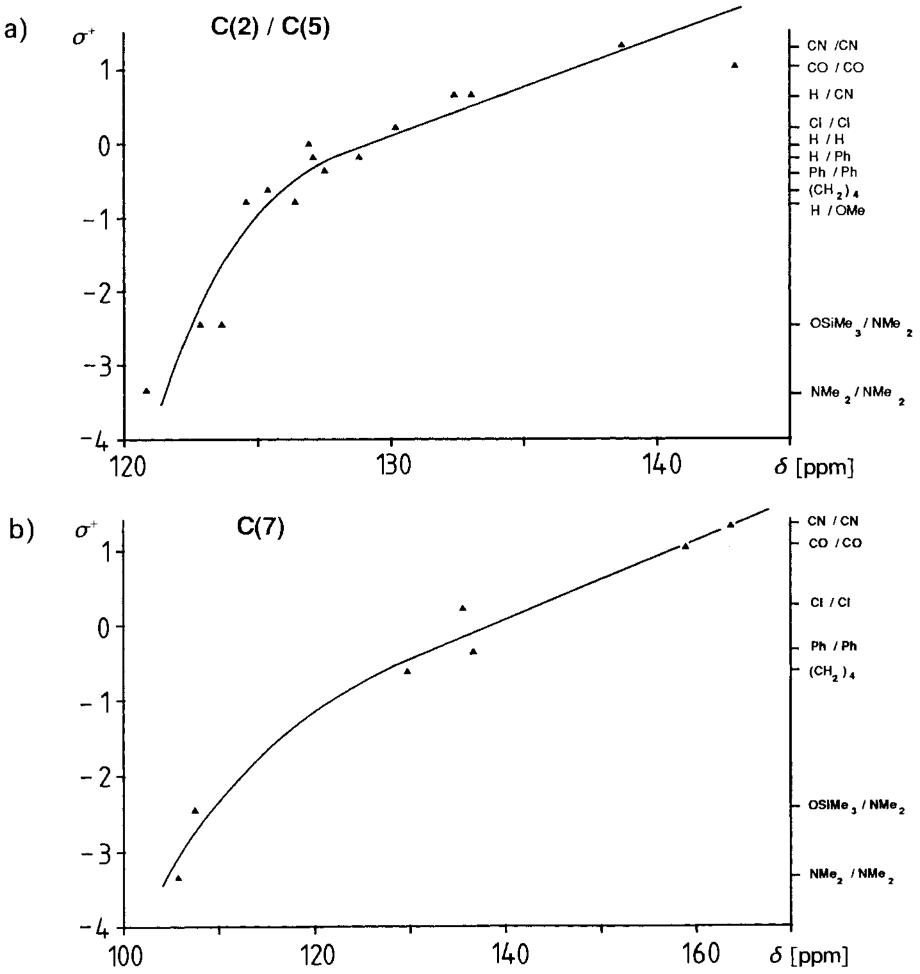

Fig. 4. *Plots of* σ^+ vs. *^{13}C-chemical shifts of C(2)/C(5)*[8]) (a) *and C(7)*[10]) (b) *of heptafulvenes*[9])

they are an ideal probe for the investigation of charge-density effects in olefinic and aromatic molecules of similar steric environment. For instance, in monosubstituted benzenes, the observed chemical shifts of *p*-C-atoms correlate well with the total charge density calculated by CNDO/2 [36], and good correlations with *Hammett* σ^+ constants have been obtained [37]. Recently, we showed that for pentafulvenes systematic high-field shifts of ^{13}C-chemical shifts of the ring C-atoms are induced by electron-donating substituents placed at the exocyclic C(6). These shifts strongly decrease in the series C(5) > C(2)/C(3) > C(1)/C(4) (see *formula* **2**) and, according to MNDO calculations, mainly reflect changes in π-charge density. For exocyclically bridged pentafulvenes, linear correlations of σ^+ *vs.* δ plots of C(1)/C(4) and C(2)/C(3) have been observed [11].

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[10]) Since steric effects may strongly falsify results, only δ(C(7)) of 8,8-disubstituted heptafulvenes has been plotted.

^{13}C-chemical shifts of heptafulvenes **3a**–**3l** as well as of cycloheptatriene **4a** and tropylium ion **5a** are listed in *Table 6*. A first glance shows that all nuclei besides C(1)/C(6) are strongly influenced by exocyclic substituents: with increasing electron-withdrawing capacity of exocyclic substituents all the ring C-atoms besides C(1)/C(6) experience a low-field shift in the series **3l** → **3d** and **3c** → **3a**, while C(8) is shifted to high field[11]). This is exactly the trend expected for a decrease in π-charge density, favoring the dipolar aromatic structure **3B**. The substituent effect decreases in the series C(7) > C(2)/C(5) > C(3)/C(4) > C(1)/C(6). This sequence is in good agreement with MNDO calculations [34]. In the case of C(1)/C(6), small charge-density effects are obscured by steric effects, and therefore, no systematic trend is observed. Also C(7) is affected by steric influences, but if 8,8-disubstituted heptafulvenes are compared[9]), then strong electronic influences of the substituents are observed (*Fig. 4b*): with increasing electron-withdrawing capacity, C(7) experiences a strong low-field shift from 105.7 ppm for **3l** to 165.2 ppm for **3d**. The maximum difference $\Delta\delta$ decreases from 59.5 ppm for C(7) to 22.0 ppm for C(2)/C(5) and to 11.8 ppm for C(3)/C(4). It is interesting to see that in all the plots of σ^+ *vs.* ^{13}C-chemical shifts of C(7), C(2)/C(5), and C(3)/C(4), no linear correlations covering all the data are obtained. All these C-atoms show a more pronounced low-field shift for strong electron-withdrawing groups (see *Figs. 4a, 4b*). This result is compatible with conformational changes in the seven-membered ring, it reflects the ring-flattening, occurring in the series **3l** → **3d** (see *Table 1*): for inversely polarized heptafulvenes existing in a boat conformation π overlap will be reduced so that substituent effects will be smaller than expected for the same but planar fulvenes **3**. With increasing ring flattening and maximum π overlap, the full electronic substituent effect will be operative.

It is interesting to see that C(8) shows a very strong but opposite trend compared with the ring C-atoms: electron-withdrawing substituents at C(8) like Cl or CO-R effect a high-field shift, while π donators like Me_2N effect a low-field shift. This is in full agreement with an increasing importance of dipolar form **3B** in the series **3l** → **3i** → **3d**, just inducing a negative partial charge at C(8), and in fact this trend is predicted by MNDO calculations. The effect is clearly observed, if fulvenes with similar steric requirements like **3l**, **3i**, and **3f** are compared[11]). δ(C(8)) of fulvenes **3d** and **3e** is not typical due to the anisotropy effect of the CN groups.

If polar heptafulvenes **3e** and **3f** are compared, then it turns out that both pairs of C-atoms C(2)/C(5) and C(3)/C(4) of **3f** (R^1,R^2 = CO–$(CH_2)_2$–CO) absorb at higher frequency than expected from σ^+ constants[12]), although both compounds are planar according to X-ray results. The conclusion is that charge separation as well as bond-delocalization[12]) are more pronounced in **3f** than expected. It seems that heptafulvene **3f** is special due to some sort of H-bonding between H–C(1) and H–C(6) with the coplanar CO groups possibly leading to a larger σ^+ value for the CO group (see later): the 'bond-lengths' O–H–C(1) and O–H–C(6) are in the range of 2.065 Å, while the bond-length of C(7)–C(8) (1.407 Å) is markedly reduced compared with that of **3l** (1.442 Å) [38].

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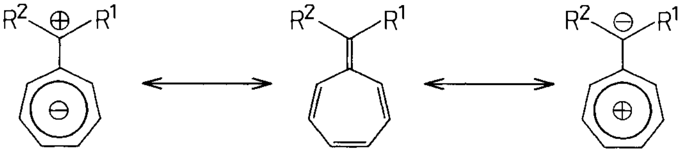
[11]) Although the trend of C(8) is obvious, correlations of σ^+ *vs.* δ are useless, because C(8) is strongly influenced by steric effects and anisotropy effects (*e.g.* of CN groups) of substituents.

[12]) The same effect is seen in *Table 3*: compared with **3e** ($R^1 = R^2$ = CN), *J*(2,3)/*J*(4,5) of **3f** (R^1,R^2 = CO–$(CH_2)_2$–CO) is larger, while *J*(3,4) is smaller than expected. This hints to the conclusion that alternation of bond lengths is reduced in **3f** compared with **3e**, a result which is confirmed by the X-ray results!

Substituent effects are additive insofar that 8-monosubstituted and 8,8-disubstituted heptafulvenes with a similar $\Sigma\sigma^+$ also absorb in a similar δ range. For example, C-atoms C(2) and C(5) of **3c** with $\sigma^+ = -0.78$ absorb at 126.4 and 129.8 ppm, while the same C-atoms of **3j** with $\Sigma\sigma^+ = -0.62$ absorb at 125.4 and 131.0 ppm, respectively. Furthermore, the results of *Table 6* show that substituents at C(8) have the same effect on both sides of the seven-membered ring. This is very clear from the spectra of 8-monosubstituted and unsymmetrically disubstituted heptafulvenes, where the pairs of atoms C(2)/C(5) and C(3)/C(4) absorb within 2 ppm[13]). Once again, the results are compatible with a symmetric boat conformation (for unpolar heptafulvenes) and a planar ring conformation (for polar heptafulvenes).



3C **3A** **3B**

Finally, the question is at stake, whether it is justified to speak of 'inversely polarized heptafulvenes' in the case of **3k** or **3l** bearing strong electron-donating groups at C(8) [22]. If heptafulvenes **3l** ($R^1 = R^2 = Me_2N$) and **3f** ($R^1,R^2 = CO-(CH_2)_2-CO$) are compared (see *Table 6*), then there is no doubt that the exocyclic double bond C(7)=C(8) of **3l** experiences a strong inverse polarization, with C(7) at 105.7 ppm instead of 158.9 ppm for **3f** and C(8) at 157.5 ppm instead of 114.5 ppm for **3f**. However, it is interesting to look at C-atoms C(2)/C(5) which so far have not been checked [22] due to ambiguous assignments. Since X-ray results clearly show that the seven-membered ring deviates out-of-plane in order to avoid contributions of the energy-increasing antiaromatic structure **3C**, it is questionable at first sight, whether electron-donating groups at C(8) of heptafulvenes are still able to increase negative charge at C(2)/C(5) and C(3)/C(4). Inspection of C-atoms C(2)/C(5) of 'inversely polarized' **3l** with unpolar **3g** clearly shows a $\Delta\delta$ value of −9.3 ppm which implies that the charge-density effect is experienced at C(2)/C(5) of **3l**. On the other hand, the effect is hardly seen for C(3)/C(4) with a $\Delta\delta$ of −1.6 ppm due to the scattering of ^{13}C-chemical shifts and the decrease of charge-density effects in the series C(7) > C(2)/C(5) > C(3)/C(4). However, within the limitations imposed on ^{13}C-NMR interpretation, one can conclude that it is justified to distinguish a special class of 'inversely polarized heptafulvenes' [22]. This class is characterized by a high-field shift of the ring C-atoms and a low-field shift of C(8) compared with 'normally polarized heptafulvenes' like **3f** or unpolar heptafulvenes like **3h** or **3g**. It is very clear from X-ray results, however, that 'inversely polarized heptafulvenes' will not be planar thus avoiding strong contributions of antiaromatic forms of type **3C** to the ground state.

7. Substituent Effect on ^{13}C,^{13}C-Coupling Constants (see *Table 7*). – ^1J(C,C) Coupling constants could be an attractive tool for the investigation of cyclic cross-conjugated molecules, because they are strongly dependent on bond lengths [39]. Other factors

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[13]) Differences $\Delta\delta$ between pairs C(1)/C(6) are expected to be larger due to steric effects.

affecting ${}^1J$(C,C) values are hybridization electronegativity of substituents as well as the number of substituents at a given C-atom [39]. Keeping in mind that substituents at C(8) of heptavulvenes **3** are far away from the ring-C-atoms C(2)–C(5), it is reasonable to assume that these additional effects should be quite small. In this case, substituent effects influencing bond lengths (or π delocalization) could be directly derived from ^{13}C,^{13}C-coupling constants. Very recently, this has been shown for pentafulvenes **2** [12]. The main difference between **2** and **3** is that the ring system of **2** is invariably planar while substituents at C(8) may influence the conformation of **3** (see *Table 1*).

${}^1J$(C,C) Values of a series of heptafulvenes **3** are listed in *Table 7*. The results show that the substituent-induced trends are considerably more complicated than expected. Although the coupling constants of unpolar **3i** are clearly alternating and are very similar to those of **4a** or of butadiene [39][14]), the substituent-induced trends of coupling constants are rather surprising: while couplings over formal single bonds J(2,3)/J(4,5) and J(1,7)/J(6,7) are expected to increase in the row **3k** → **3d** (since bond-lengths are decreasing), they are decreasing! On the other hand, couplings over formal double bonds are expected to moderately decrease in the series **3k** → **3d**, while in reality they are strongly decreasing. A possible explanation says that ${}^1J$(C,C) coupling constants are strongly affected by changes of π-charge density and/or C–C–C bond angles. The conclusion is that, contrary to pentafulvenes **2**, ${}^1J$(C,C) coupling constants do *not* give reliable informations concerning substituent-induced changes of bond lengths of heptafulvens **3**.

8. Discussion. – Recent results of pentafulvenes **2** showed that both ${}^3J$(H,H) and ${}^1J$(C,C) coupling constants as well as ^{13}C-chemical shifts are systematically influenced by exocyclic substituents [11] [12]: with increasing electron-donating capacity of R^1, R^2, ${}^3J$(H,H) and ${}^1J$(C,C) coupling constants of ring protons and ring-C-atoms are approaching, and linear correlations of the NMR parameters *vs.* σ^+ or calculated bond lengths are obtained. This is easily explained with an increasing π delocalization in the five-membered ring due to the importance of **2B**. Furthermore, the dipolar form **2B** suggests a substituent-induced increase of π charge-density of the ring-C-atoms, which is convincingly shown by the high-field shift of the ring-C-atoms. Additionally, in agreement with MNDO calculations, the effect decreases in the series C(5) > C(2)/C(3) > C(1)/C(4), and linear regressions of δ values with σ^+ are observed.

The NMR results presented here show that the behavior of heptafulvenes **3** is more complicated than that of pentafulvenes **2**. There are pronounced effects of substituents R^1, R^2 on all the NMR parameters of heptafulvenes, and in most cases the induced trends are in the expected direction, however, *in no case linear correlations with* Hammett *substituent constants σ^+ are observed over the whole range of substituents*. Our interpretation, being in agreement with X-ray results, is that a symmetrical boat conformation is important for inversely polarized heptafulvenes of the type **3k** and **3l**, while, with increasing electron-withdrawing capacity of the substituents, ring planarization has to take place, before the substituents can develop their full electronic effect. So several effects are influencing NMR parameters of heptafulvenes, the most important being the extent of ring planarization as well as of π delocalization. While steric effects of different substituents R^1, R^2 are hampering the interpretation of the NMR results of C(1), C(6), C(7),

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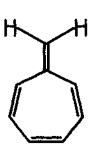
[14]) ${}^1J$(C,C) Values of butadiene: $J(1,2) = 68.1$ and $J(2,3) = 53.75$ Hz.

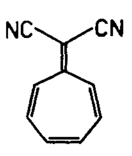
C(8), and H–C(1)/H–C(6), minor effects accompanying ring-planarization are changes of C–C–C and H–C–C bond angles.

Another tiresome problem hampering reliable NMR interpretation is the sometimes pronounced scattering of NMR data (see *Tables* and *Figs.*). If the origin of the scattering is well known, one can correct for it. Since it is reasonable to assume that steric effects are influencing δ(C(7)), correction parameters may be applied [40], so that δ(C(7)) of heptafulvenes but with a similar steric environment are calculated.

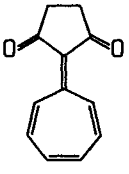
On the other hand, it is clear from ^3J(H,H) couplings as well as from ^{13}C-chemical shifts that heptafulvenes **3f** (R^1–R^2 = CO–$(CH_2)_2$–CO) and **3d** (R^1 = CF_3CO, R^2 = CN) are more delocalized than they should be according to substituent constants σ^+. This is confirmed for **3f** by X-ray results: although **3f** should be slightly less delocalized than **3e** (R^1 = R^2 = CN) according to *Hammett* constants σ^+, a comparison of X-ray data of both compounds shows that bond lengths alternate more in the case of **3e**. New approximate substituent constants for the CO groups at C(8) of heptafulvenes **3f** and **3d** are derived in the following way:



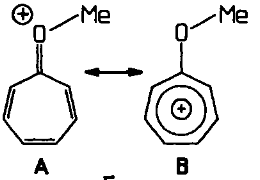
3h



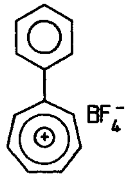
3e



3f



5a



5c

	3h	3e	3f	5a
J(2,3)	7.51	8.27	8.39	9.19 Hz
J(3,4)	11.53	10.88	10.45	9.93 Hz

It is clear from *Table 3* that ^3J(H,H) coupling constants J(2,3)/J(4,5) and J(3,4) of heptafulvenes are systematically approaching from **3h** to **3f** due to an increasing π delocalization. The trend is continued for methoxytropylium salt **5a**, but coupling constants J(2,3)/J(4,5) and J(3,4) (and appropriate bond lengths) are still slightly alternating due to some contribution of the covalent form **5A**. If the average of both coupling constants of 9.19 and 9.93 Hz is taken, then one might expect a $J(2,3) = J(3,4) = J(4,5)$ of 5.56 Hz for a completely delocalized tropylium salt **5**. It is nice to see that for heptafulvenes **3h**, **3g**, **3a**, and **3e**[15]) linear extrapolations of plots of σ^+ *vs.* J(2,3)/J(4,5) and J(3,4), respectively, cross at a very similar average; horizontally, this corresponds to a σ^+ of approximately 3.0.

Of the heptafulvenes **3h** [6] and **3f** [2] as well as of phenyltropylium salt **5c** [15], the bond lengths are known, and all the mentioned compounds were shown to be planar. A reasonable term of bond-length alternation in the seven-membered ring is $\Delta r = r(1,7) + r(2,3) - r(1,2) - r(3,4)$, which amounts to 0.221 (**3h**), 0.128 (**3f**), and 0.043 Å (**5c**). Now the σ^+ constants of the substituents of **3h** ($\sigma^+ = 0$) and of **5c** derived above ($\sigma^+ \approx 3.0$) may be plotted *vs.* the Δr values obtained from MW and X-ray results. Since a linear plot is expected for planar compounds **3h**, **3f**, and **5c**, a $\Delta r = 0.128$ Å of **3f**

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[15]) Similarly to pentafulvenes **2** [11], linear plots of σ^+ *vs.* ^3J values or bond lengths are expected for *planar* heptafulvenes. According to MW (**3h**) and X-ray data (**3e**), the extreme members of the series are planar, so that a linear extrapolation is justified.

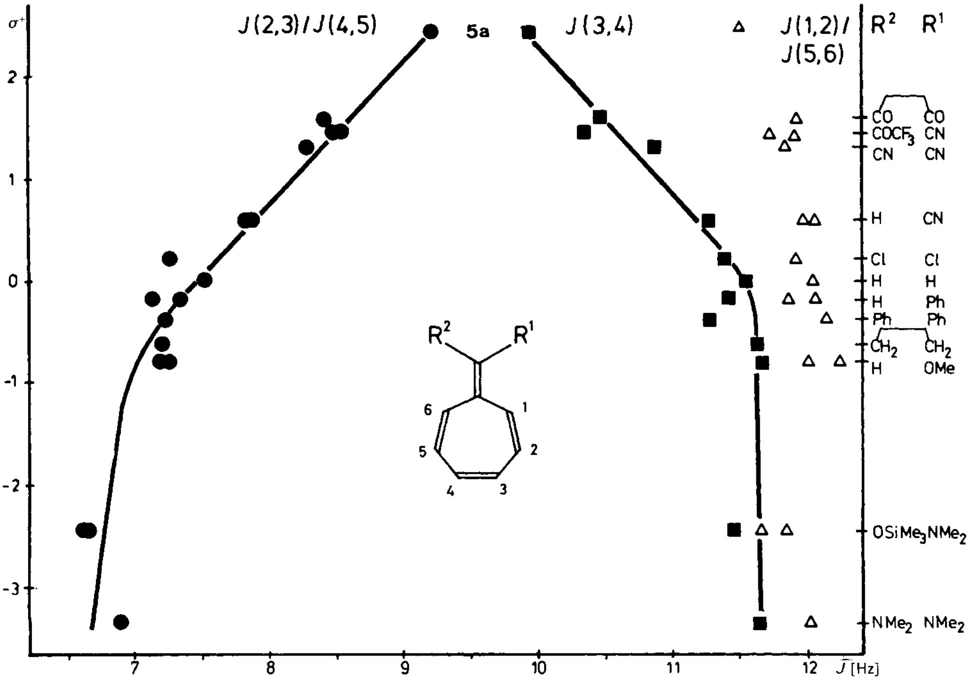

Fig. 5. *Modified plot of* σ^+ vs. $^3J(H,H)$ *coupling constants of heptafulvenes* **3** *as well as of methoxytropylium salt* **5a**[16])

corresponds to a total σ^+ of +1.56 for two CO groups or to a σ^+ of 0.78 per CO group of heptafulvenes[6]).

The modified plot of σ^+ *vs.* ^3J values including an expansion of the σ^+ scale as well as revised σ^+ constants for CO groups[16]) is given in *Fig. 5*. It clearly shows that with increasing electron-withdrawing capacity of the substituents $J(2,3)/J(4,5)$ and $J(3,4)$ are approaching and, as discussed earlier, that both sets of coupling constants are nearly insensitive ($J(3,4)$) or only moderately increasing ($J(2,3)/J(4,5)$) for non-planar inversely polarized or unpolar heptafulvenes. The new result is that, despite of some scatter, there seems to exist a linear dependancy of both coupling constants in the range from **3h** ($R^1 = R^2 = H$) to strongly polarized heptafulvenes of type **3e** and **3f** and even to tropylium salts **5**. This perfectly matches the expected influence of substituents on ^3J values of planar heptafulvenes; indeed, all these compounds have shown to be planar according to MW (**3h**) and X-ray results (**3e**, **3f**, and **5c**). The only surprising behavior is shown by $J(1,2)/J(5,6)$ which only slightly varies from polar **3f** (11.91 Hz) to tropylium salt **5a** (11.40 Hz)[17]). This behavior is not expected according to accessible X-ray data, and it cannot be explained so far.

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[16]) Compared with *Fig. 3*, the modification consists in the application of revised σ^+ values for the heptafulvenes **3d** and **3f** with CO groups, as well as in an expansion of the σ^+ scale by using ^3J values of the tropylium salt **5a**.

[17]) On the other hand, both sets of coupling constants $J(1,2)/J(5,6)$ and $J(3,4)$ are of the same size and behave similarly in the range of unpolar to inversely polarized heptafulvenes.

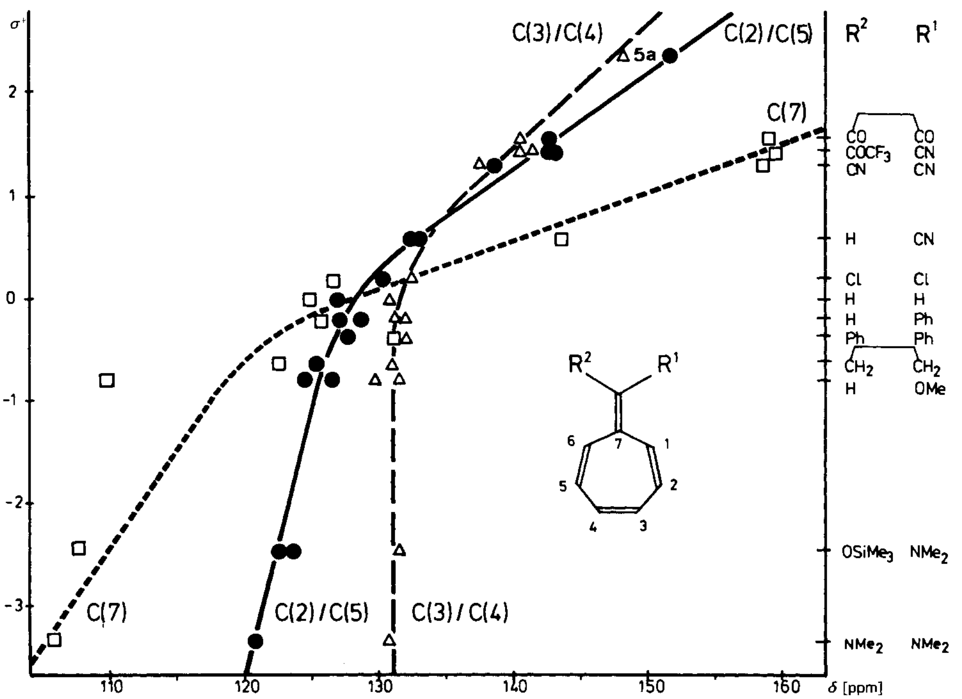

Fig. 6. *Modified plot of* σ^+ vs. *^{13}C-chemical shifts of C(7), C(2)/C(5), and C(3)/C(4) of heptafulvenes* **3** *as well as of methoxytropylium salt* **5a**[18])

The modified plot of σ^+ *vs.* ^{13}C-chemical shifts including an expansion of the σ^+ scale, revised σ^+ constants for CO groups and substituent corrections for C(7)[18]) is shown in *Fig. 6*. Due to a strong scattering of C(7) of heptafulvenes **3c** (R^1 = MeO, R^2 = H) and **3i** ($R^1 = R^2$ = Ph), there is not a very good correlation of δ(C(7)), but there are good correlations for C(2)/C(5) and C(3)/C(4)[19]). There are two ranges of different sensitivity, namely a comparably unsensitive range, varying from inversely polarized to unpolar heptafulvenes, as well as a sensitive range, varying from unpolar to polar heptafulvenes and to tropylium salts. In both ranges, the substituent-induced high-frequency shifts decrease in the series C(7) > C(2)/C(5) > C(3)/C(4). While C-atoms C(3)/C(4) are nearly uninfluenced in the range of negative σ^+ values, no substituent effect is observed for C(1)/C(6) in the whole range[19]). The new result is that there seems to be a linear relationship in the polar range for all sets of C-atoms plotted in *Fig. 6*. In fact, linear plots may be expected for planarized heptafulvenes according to MNDO calculations, as soon as ^{13}C-chemical shifts are dominated by charge-density effects, and are really observed for planar pentafulvenes [11].

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[18]) Compared with *Figs. 4a* and *4b*, the modification consists in the application of revised σ^+ values for heptafulvenes **3d** and **3f** with CO groups, as well as in an expansion in the σ^+ scale by using data of **5a**. Furthermore, δ(C(7)) has been corrected for the different substitution pattern of the exocyclic double bond according to [40]. All the δ values of C(2)/C(5) and C(3)/C(4) are unchanged and taken out of *Table 5*.

[19]) C-atoms C(1)/C(6), which are not shown in the plot, are nearly uninfluenced by electronic effects of substituents and scatter around 135 ± 4 ppm (see *Table 6*) due to steric effects.

Summarizing, *Figs. 5* and *6* clearly reveal that heptafulvenes **3** show two ranges of substituent induced behavior: ^3J(H,H) coupling constants as well as ^{13}C-chemical shifts of the ring atoms are relatively unsensitive to 'inversely polarizing substituents' R^1 and R^2. On the other hand, strong electron-withdrawing substituents R^1, R^2 induce an approach of H,H coupling constants J(2,3)/J(4,5) and J(3,4) as well as a pronounced high-frequency shift of ring-C-atoms decreasing in the series (C(7) > C(2)/C(5) > C(3)/C(4). Furthermore, *Figs. 5* and *6* hint at linear correlations of σ^+ *vs.* ^3J(H,H) and σ^+ *vs.* $\delta(^{13}C)$ in this range.

From the preceding NMR investigations as well as from X-ray data, it is evident that the conformation of heptafulvenes is strongly influenced by exocyclic substituents. These data as well as MNDO calculations suggest that the following energy terms mainly influence the conformation of heptafulvenes: π-delocalization energy, core-core repulsion, ring-strain energy, and steric interactions. As by spectroscopic investigations, always the sum of these effects is detected, it is difficult to estimate the amount of the individual energy terms contributing to the total energy. In the following, the influence of these energy terms on the conformation of heptafulvenes is qualitatively discussed. To obtain more precise information about individual terms, MNDO calculations [34] of **3a**, **3e**, **3f**, **3h**, **3j**, and **3l**, both in a bond-alternant planar and in a boat conformation, were performed.

Delocalization Energy. With increasing electron-withdrawing character, π-delocalization energy increases, thus lowering the ground-state energy of the planar molecule. On the other hand, in a hypothetical planar antiaromatic conformation **3C**, a negative delocalization energy is expected for electron-donating groups. Here, a boat conformation with reduced π-overlap is energetically more favorable. Another important driving force favoring a planar conformation of type **3A** seems to be *core-core repulsion* [41]: MNDO calculations show that *Coulomb* interaction between ring-C-atoms is reduced in a planar conformation. Especially for $-M/-I$ substituents – inducing a partial positive charge in the ring – this energy term would be high in a hypothetical boat conformation. It is, therefore, a driving force for planarity in the case of heptafulvenes with electron-withdrawing substituents. For inversely polarized heptafulvenes with a partial negative charge in the ring, the importance of this energy term is reduced.

Ring-Strain Energy. It is favoring a boat conformation as C—C—C bond angles are disturbed in a planar seven-membered ring compared to an open-chain polyene. A decrease of bond alternation seems to be accompanied by a further increase of this term.

Steric Interactions. Steric interactions between exocyclic substituents and the ring are strongly dependent on the size of the exocyclic groups. For large substituents, the interactions are reduced in a boat conformation. But even in a planar conformation, energy can alternatively be lowered by an increase of the bond length (C(7)—C(8) and a decrease of the bond angles R^1—C(8)—R^2 and C(1)—C(7)—C(8). These effects are observed for **3e** [41].

The resulting conformation is determined by the relative size of these energy terms. Ring strain and steric interactions favor a boat conformation, while π delocalization and internuclear repulsion tend to a planar molecule in the case of electron-withdrawing groups. In fact, heptafulvenes **3** with strong electron-withdrawing groups are planar according to X-ray results, so that the π system experiences the full electronic effect of the substituents R^1 and R^2. Therefore, it is not surprising that in this range NMR parameters like ^3J(H,H) coupling constants or ^{13}C-chemical shifts – which show linear correlations *vs.* σ^+ for planar pentafulvenes – are linearly dependent on *Hammett* substituent constants σ^+

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Experimental Part

Syntheses. – Heptafulvenes **3a** [42], **3b** [21], **3c** [43], **3d** [44], **3e** [45], **3f** [2], **3g** [2], **3h** [2], **3i** [41], **3j** [2], **3k** [2], **3l** [23], cycloheptatriene **6a** [46], and tropylium ion **5a** [47] have been prepared according to literature procedures.

NMR Spectra. – ^{1}H-NMR spectra of carefully filtered and degassed soln. of heptafulvenes **3a**, **3b**, **3c**, **3e**, **3f**, **3g**, **3i**, **3k**, **3l**, of cycloheptatriene **6a**, and of tropylium ion **5a** (at ambient temp.) and **3d** (10°), **3h** (−20°). **3j** (−30°) were measured in (D$_6$)acetone, where highest resolution was obtained, with a *Bruker AM 400* spectrometer. Typical parameters to achieve high-resolution spectra, being necessary for a successful spin analysis, were: spectral width 500 Hz, 16 K data points, corresponding to a digital resolution of 0.06 Hz/Pt, acquisition time 16.4 s, pulse width 13 µs. For resolution enhancement, a *Gaussian* function was used with a line broadening of −0.2 Hz and a *Gaussian* constant of 0.15. The FID was zero-filled to 32 K prior to *Fourier* transformation. For simulations and iterations, the program *PANIC* was used [30]. Calculations were performed on a computer of the type *Aspect* 1000 equipped with 256 kByte memory, a multicolor display, floppy-disc FDD 280, HD 160 hard-disc, and a *Watanabe WX 4731* digital plotter. The strategies used for the analysis of the *AA'MM'XX'*, *AA'MM'XX'YY'*, and of the high-order non-symmetric 6- and 7-spin systems are described in [29].

^{13}C-NMR spectra have been recorded in CDCl$_3$ soln. at ambient temp. except for **3c**, **3g**, **5a** ((D$_6$)acetone); **3h** (−20°); **3j** (−30°). Assignments were based on reference compounds and checked by 'off-resonance' decoupled ^{13}C spectra and ^{13}C,^{1}H-correlated 2D spectra [48].

^{13}C,^{13}C-coupling constants were determined by broad-band-decoupled ^{13}C spectra and 1D-INADEQUATE spectra [31], for cases with signal overlapping, using concentrated (> 100 mg) CDCl$_3$ solns. at ambient temp.

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