113. ^{1}H- and ^{13}C-NMR Investigation of Pentafulvenes[1])

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^{1}H- and ^{13}C-NMR spectra of a series of 6-(*p*-X-phenyl)pentafulvenes **1**–**9** as well as of 6-R-substituted and 6,6-R^{1},R^{2}-disubstituted pentafulvenes **10**–**23** have been analysed. It turns out that the π-system of pentafulvenes is an attractive probe for the investigation of electronic substituent effects. Changes of *vicinal H,H-coupling constants* with increasing electron-donating capacity of the substituents X and R are interpreted in terms of an increasing π delocalisation in the 5-membered ring, and linear correlations of *Hammett* substituent constants σ_p^+ or MNDO-calculated C–C bond lengths and ^{3}J values are observed. On the other hand, a systematic high-field shift of *^{13}C chemical shifts* of the ring C-atoms is induced by electron-releasing substituents R and X, which decreases in the series C(5) > C(2)/C(3) > C(1)/C(4), and which mainly reflects changes in π-charge density.

1. Introduction. – The π-system of pentafulvene could be an attractive probe for the investigation of electronic substituent effects in cross-conjugated molecules, especially if changes in charge density and charge delocalisation were easily accessible. ^{1}H- and ^{13}C-NMR spectra of unsubstituted pentafulvene as well as of a series of substituted pentafulvenes have been analysed and assigned by *Philipsborn* and coworkers [2]. The results showed that ^{1}H chemical shifts are influenced by a variety of effects, whereas the size of the vicinal H,H-coupling constants qualitatively reflects the extent of bond delocalisation. On the other hand, ^{13}C chemical shifts of pentafulvenes are strongly influenced by substituents at C(6), and the substantial high-field shift of C(2) and C(3) of 6-(dimethylamino)pentafulvene has been interpreted in terms of a charge density effect [2].

To investigate the influence of substituents on the π-system of pentafulvenes in an invariant steric environment, we synthesized a series of 6-(*p*-X-phenyl)pentafulvenes **1**–**9**. In [3], we reported that, in fact, electronic substituent effects induce systematic changes of ^{13}C chemical shifts as well as of vicinal coupling constants in the 5-membered ring. We showed that both parameters give linear correlations if plotted *vs.* *Hammett* substituent constants σ. Very recently, the ^{13}C-NMR spectra of a series of 6-methyl-6-(*p*-X-phenyl)pentafulvenes have been investigated by *Sardella et al.* [4]. Despite of some assignment problems and smaller effects compared with 6-(*p*-X-phenyl)pentafulvenes, a similar trend of substituent-induced ^{13}C chemical shifts of fulvene C-atoms has been observed [4].

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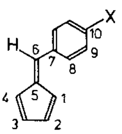
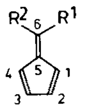
[1]) Fulvenes, Fulvalenes, Part 49; for Part 48: [1].



1 $X = NO_2$
2 $X = CN$
3 $X = Br$
4 $X = Cl$
5 $X = F$
6 $X = H$
7 $X = CH_3$
8 $X = CH_3O$
9 $X = (CH_3)_2N$



10 $R^1 = (CH_3)_3C, R^2 = H$
11 $R^1 = CH_3O, R^2 = H$
12 $R^1 = (CH_3)_2N, R^2 = H$
13 $R^1 = R^2 = CH_3$
14 $R^1 = R^2 = CH_3S$
15 $R^1 = R^2 = CH_3O$
16 $R^1 = (CH_3)_2N, R^2 = CH_3S$

17 $R^1 = (CH_3)_2N, R^2 = C_2H_5O$
18 $R^1 = R^2 = (CH_3)_2N$
19 $R^1, R^2 = -CH{=}CH-CH{=}CH-$
20 $R^1, R^2 = -(CH_2)_4-$
21 $R^1, R^2 = -S-(CH_2)_2-S-$
22 $R^1, R^2 = -O-(CH_2)_2-O-$
23 $R^1, R^2 = -\underset{CH_3}{N}-(CH_2)_2-\underset{CH_3}{N}-$

Here, we report the results of our ^1H- and ^{13}C-NMR investigation of 6-(*p*-X-phenyl)-pentafulvenes [5] in comparison with a series of selected 6-monosubstituted and 6,6-disubstituted pentafulvenes [5] as well as with pentafulvalene **19** [6].

2. General Remarks. – Whereas ^1H-NMR spectra of 6-monosubstituted pentafulvenes are very complex at 100 MHz [2], in most cases approximate first-order spectra are obtained at 400 MHz. Expanded multiplets of the ring protons of 6-(*p*-methoxyphenyl)-pentafulvene (**8**) are shown in *Fig. 1*. With respect to the assignment, H–C(2) acts as key-proton which is easily located due to its large (1.5–1.6 Hz) $^5J_{tt}$ long-range coupling with H–C(6) [2]. Sets of chemical shifts and coupling constants obtained after computative simulation and iteration are given in *Tables 1* and *3*. According to *Table 1*, δ-values of 6-(*p*-X-phenyl)pentafulvenes are only slightly affected by solvent changes from $CDCl_3$ to (D_6)acetone. However, resolution is considerably influenced by solvents and was by far the best in (D_6)acetone. Solvent influences on H,H-coupling constants have been checked for **9** ($X = N(CH_3)_2$), and they are found to be very small: changing from $CDCl_3$ to (D_6)acetone, the largest difference was 0.05 Hz, the average difference 0.025 Hz.

^1H-NMR spectra of 6,6-disubstituted pentafulvenes **13**–**23** display *AA'XX'* or *AA'BB'* pattern at 80 MHz and ambient temperature. This is at first sight surprising for **16** and **17** bearing different substituents at C(6). In these cases, rotation around the central C(5)=C(6) bond is fast enough at ambient temperature. In (D_6)acetone solutions of **16**, coalescence of the ring protons is observed at –38° (80 MHz), corresponding to a $\Delta G^{\neq}$ value of 11.8 kcal/mol.

At –90°, an *ABXY* spectrum is observed for (D_6)acetone solutions of **16**, while **17** still displays an *AA'BB'*-type spectrum, in agreement with earlier observations [7]. Qualitatively, the free activation energy for the rotation around the central double bond very reasonable decreases in the series **12** [7] [8] > **16** > **17**, thus, with increasing electron-donating capacity of the exocyclic substituents.

Chemical shifts of pentafulvenes **10**–**23** are listed in *Table 2*. Assignments of pairs of ring protons have been checked by NO-experiments: Irradiation of the exocyclic methyl groups induces a nuclear *Overhauser* effect of the high-frequency multiplets of **14** (27%, $CDCl_3$), **15** (23%, (D_6)acetone), **18** (21%, (D_6)acetone), and **23** (34%, $CDCl_3$). In the case of 6,6-dimethylfulvene **13**, the assignment of the low-frequency multiplet at 6.38 ppm to protons H(C–2)/H(C–3) follows from the characteristic line-broadening due to a small long-range coupling with the Me groups. For **20** and **21**, assignments are arbitrary and could be interchanged. δ-Values of 6,6-disubstituted pentafulvenes are only moderately influenced by solvent changes from (D_6)acetone to $CDCl_3$; in most cases the shift difference is smaller than 0.1 ppm, and only for polar pentafulvenes like **15** and **17**, high-frequency shifts up to 0.25 ppm are observed. As usual solvent effects are more pronounced in C_6D_6.

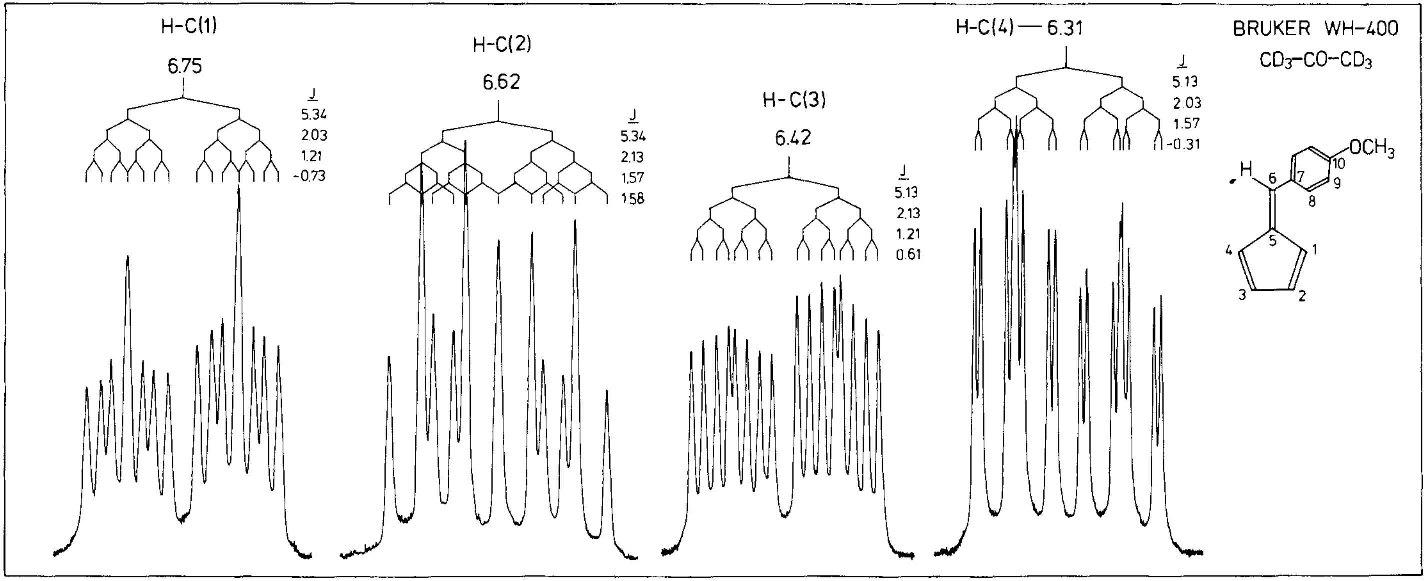


Fig. 1. *Part of the* ^{1}*H-NMR spectrum of 6-(* p*-methoxyphenyl)pentafulvene* (**8**) (multiplets of H–C(1)–H–C(4), 400 MHz, (D$_6$)acetone)

Coupling constants of pentafulvenes **13–23** are given in *Table 4*. Solvent effects on H,H-coupling constants have been checked for **16** and **21** and found to be within the experimental error, even if (D_6)acetone is replaced by C_6D_6.

^{13}C-NMR spectra of a series of pentafulvenes have been analysed by *Philipsborn* and coworkers [2]. The assignments of **13–18** and **21–23** *(cf. Table 7)* are based on this work, they have been confirmed for **23** by selective ^{1}H,^{13}C-decoupling experiments. For the assignment of **19**, see [6]. ^{13}C-NMR spectra of 6-(*p*-X-phenyl)pentafulvenes **1**, **3**, **8** and **9** *(Table 6)* have been assigned by various methods including relative intensities, selective ^{1}H, ^{13}C decoupling experiments as well as calculation of increments of aromatic C-atoms [9].

3. Substituent Effects on ^{1}H Chemical Shifts (see *Tables 1* and *2*). – It is well-known that ^{1}H chemical shifts of vinylic protons are influenced by several factors including charge-density, anisotropy, and *van-der-Waals* effects. Electron-releasing substituents at C(6) of pentafulvenes are expected to increase the π-electron density of the ring and, in absence of other effects, to induce a shift of ring protons towards lower frequencies.

Table 1. *^{1}H Chemical Shifts of 6-(*p*-X-Phenyl)fulvenes* (31°, ±0.01 ppm with respect to TMS)

Compound	X	in $CDCl_3$					in (D_6)Acetone				
		H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(6)	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(6)
1	NO_2	6.53	6.68	6.53	6.29	7.17	6.68	6.71	6.53	6.35	7.39
2	CN	6.54	6.68	6.54	6.29	7.14	6.65	6.69	6.51	6.33	7.32
3	Br	6.61	6.66	6.51	6.29	7.10	6.68	6.65	6.48	6.31	7.24
4	Cl	6.61	6.66	6.49	6.27	7.13	6.68	6.65	6.47	6.32	7.26
5	F	6.63	6.66	6.50	6.30	7.14	6.69	6.65	6.46	6.32	7.26
6	H	6.68	6.64	6.49	6.30	7.18	6.72	6.65	6.48	6.34	7.29
7	CH_3	6.71	6.65	6.49	6.31	7.18	6.73	6.63	6.44	6.36	7.24
8	CH_3O	6.72	6.66	6.47	6.31	7.14	6.75	6.62	6.42	6.31	7.21
9	$(CH_3)_2N$	6.79	6.63	6.43	6.31	7.12	6.79	6.58	6.35	6.27	7.13

Table 2. *^{1}H Chemical Shifts of Pentafulvenes* ((D_6)acetone, ±0.01 ppm with respect to TMS)

Compound	R^1	R^2	Temp. [°C]	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(6)	CH_3	CH_2
10	$(CH_3)_3C$	H	30	6.65	6.53	6.32	6.14	6.45	1.28	
11	CH_3O	H	30	6.50	6.37	6.23	6.30	7.14	3.95	
12	$(CH_3)_2N$	H	30	6.48	6.33	6.11	6.26	7.20	3.15	
13	CH_3	CH_3	30	6.50	6.38	6.38	6.50		2.14	
14	CH_3S	CH_3S	41	6.51	6.35	6.35	6.51		2.52	
15	CH_3O	CH_3O	41	6.56	6.10	6.10	6.56		4.03	
16	$(CH_3)_2N$	CH_3S	41	6.48	6.18	6.18	6.48		2.33, 3.33	
17	$(CH_3)_2N$	C_2H_5O	41	6.29	6.01	6.01	6.29		1.33, 3.17	4.30
18	$(CH_3)_2N$	$(CH_3)_2N$	41	6.12	5.92	5.92	6.12		3.03	
19	CH=CH–CH=CH[a])		15	6.59	6.69	6.69	6.59			
20	$CH_2–CH_2–CH_2–CH_2$		30	6.34	6.32	6.32	6.34			1.79, 2.78
21	$S–CH_2–CH_2–S$		41	6.32	6.27	6.27	6.32			3.63
22	$O–CH_2–CH_2–O$		41	6.44	6.08	6.08	6.44			4.67
23	$N(CH_3)–CH_2–CH_2–N(CH_3)$		30	6.28	6.01	6.01	6.28		3.22	3.65

[a]) CD_2Cl_2 Soln. containing some THF.

However, if π-delocalisation in the 5-membered ring increases, the charge-density effect may be counterbalanced to some extent by the ring-current effect, so that the overall 'electronic-substituent effect' (including charge density and charge delocalisation) might be small. If, furthermore, pentafulvenes with substituents of very different steric demand are compared, no systematic trend of proton chemical shifts can be expected [10].

We tried to reduce steric effects *a)* by introducing a Ph ring as spacer between the substituent X and the fulvene unit (**1–9**); *b)* by bridging substituents at C(6) in a 5-membered ring (**19–23**). In the first case, a new problem arises, because an inspection of *Dreiding* molecular models reveals that the Ph ring is forced out-of-plane of the fulvene ring due to steric interactions between H–C(1) and H–C(8). The twist angle between the two rings has been estimated to be at about 70° for 6-methyl-6-phenylfulvene by MNDO calculations [4]; it is expected to be somewhat smaller for 6(*p*-X-phenyl)fulvenes of type **6**, and it might be influenced by the substituent X.

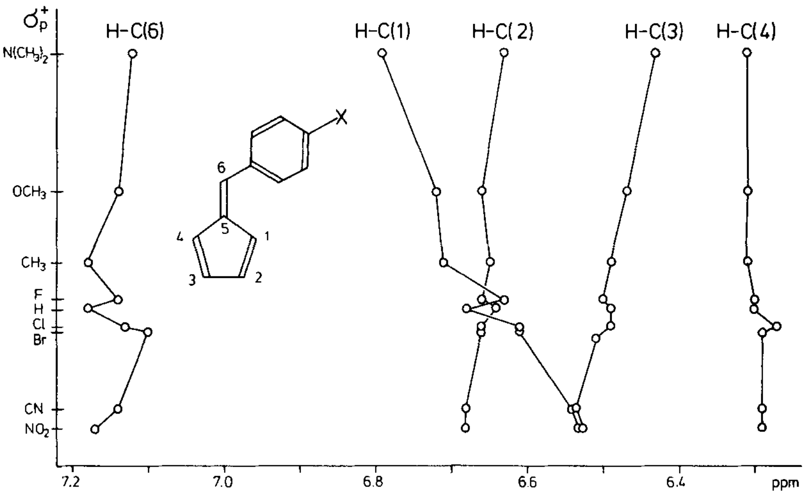


Fig. 2. *Plot of* Hammett *substituent constants* σ_p^+ vs. ^1H *chemical shifts of 6-(* p-*X-phenyl)pentafulvenes* **1–9**

Inspection of *Table 1* and *Fig. 2* demonstrates that there is no linear shift of δ values with increasing electron-releasing capacity of X (measured by the *Hammett* σ_p^+ values [11]) even for *6-(* p-*X-phenyl)pentafulvenes,* although a trend towards higher field is observed for H–C(2) and H–C(3). The most surprising feature in *Fig. 2* is the different behaviour of H–C(4) and H–C(1). Whereas H–C(4) is virtually not affected by substituents X, electron-releasing substituents X induce a remarkable low-field shift of H–C(1). This effect could be reasonably explained, if one assumes that electron-releasing groups X are increasing the π overlap of the Ph and fulvene rings, thus, reducing the twist angle between the two rings. In this case, H–C(1) would be deshielded due to the *van-der-Waals* as well as the ring-current effect.

A similar but more pronounced trend is observed for *6-substituted* as well as for *6,6-disubstituted pentafulvenes* bearing electronically different substituents at C(6), where H–C(2) and H–C(3) are shifted to higher field with increasing electron-donating capacity of R^1/R^2 (*Table 2, cf.* the series **10→12**, **13→18**, and **19→23**).

Table 3. *H,H-Coupling Constants* J_{ij} [Hz] *of 6-(*p*-X-Phenyl)fulvenes* ((D_6)acetone, ±0.02 Hz)

Compound	X	$J(1,2)$	$J(1,3)$	$J(1,4)$	$J(1,6)$	$J(2,3)$	$J(2,4)$	$J(2,6)$	$J(3,4)$	$J(3,6)$	$J(4,6)$
1	NO_2	5.44	1.22	1.97	−0.76	2.04	1.53	1.62	5.25	0.67	−0.31
2	CN	5.44	1.23	1.99	−0.76	2.03	1.53	1.58	5.22	0.67	−0.35
3	Br	5.40	1.24	1.99	−0.77	2.06	1.51	1.66	5.18	0.66	−0.33
4	Cl	5.42	1.19	2.05	−0.72	2.08	1.51	1.60	5.18	0.61	−0.29
5	F	5.39	1.20	2.00	−0.75	2.09	1.55	1.62	5.17	0.57	−0.36
6	H	5.37	1.21	2.01	−0.74	2.10	1.55	1.59	5.17	0.63	−0.33
7	CH_3	5.35	1.22	2.02	−0.72	2.11	1.56	1.57	5.13	0.65	−0.33
8	CH_3O	5.34	1.21	2.03	−0.73	2.13	1.57	1.58	5.13	0.61	−0.31
9	$(CH_3)_2N$	5.26	1.23	2.01	−0.73	2.15	1.59	1.54	5.02	0.57	−0.31

Table 4. *H,H-Coupling Constants* J_{ij} *of Pentafulvenes* ((D_6)acetone, ±0.04 Hz)

Compound	R^1	R^2	$J(1,2)$	$J(1,3)$	$J(1,4)$	$J(1,6)$	$J(2,3)$	$J(2,4)$	$J(2,6)$	$J(3,4)$	$J(3,6)$	$J(4,6)$
10	$(CH_3)_3C$	H	5.42	1.19	1.98	−0.78	2.14	1.63	1.61	5.15	0.62	−0.30
11	CH_3O	H	5.10	1.44	2.00	−0.61	2.12	1.54	1.54	5.03	0.31	−0.21
12	$(CH_3)_2N$	H	4.77	1.39	2.15	−0.52	2.51	1.88	1.02	4.50	0.25	<0.2
13	CH_3	CH_3	5.32	1.39	2.13		2.13	1.39		5.32		
14	CH_3S	CH_3S	5.17	1.50	2.07		2.07	1.50		5.17		
15	CH_3O	CH_3O	4.88	1.61	2.20		2.38	1.61		4.88		
16	$(CH_3)_2N$	CH_3S	4.72	1.63	2.21		2.45	1.63		4.72		
17	$(CH_3)_2N$	C_2H_5O	4.53	1.69	2.23		2.53	1.69		4.53		
18	$(CH_3)_2N$	$(CH_3)_2N$	4.36	1.70	2.18		2.58	1.70		4.36		
19	CH=CH–CH=CH[a])		5.41	1.32	1.98		1.99	1.32		5.41		
20	$CH_2–CH_2–CH_2–CH_2$		5.19	1.40	2.03		2.03	1.40		5.19		
21	$S–CH_2–CH_2–S$		4.95	1.43	2.16		2.16	1.43		4.95		
22	$O–CH_2–CH_2–CH_2–O$		4.75	1.63	2.08		2.31	1.63		4.75		
23	$N(CH_3)–CH_2–CH_2–N(CH_3)$		4.21	1.78	2.24		2.82	1.78		4.21		

[a]) CD_2Cl_2 Soln. containing some THF; *J* ±0.02 Hz.

4. Substituent Effects on Vicinal H,H-Coupling Constants (see *Tables 3* and *4*). – Vicinal H,H-coupling constants are strongly influenced by four parameters, namely *a)* the dihedral angle ϕ, *b)* the H–C–C bond angle θ, *c)* the electronegativity of substituents as well as *d)* the bond length r(C,C) [12]. Factors *a–c* being small or constant (and for sterically similar substituents placed at C(6) of the pentafulvene unit, they should be approximately constant), the size of H,H-coupling constants $J(1,2)$, $J(2,3)$, and $J(3,4)$ should mainly reflect the electronic influence of substituents on bond lengths of the fulvene ring. Despite of the fact that only a few X-ray structures of pentafulvenes have been determined so far, these results show that, compared with 6,6-dimethylfulvene **13** [13], the effect of electron-releasing substituents at C(6) is an increase of the length of formal double bonds as well as a decrease of the length of formal single bonds in 6,6-bis(dimethylamino)pentafulvene **18** [14]. Since there exists a linear relationship between bond lengths and vicinal H,H-coupling constants on one side [12] as well as between bond lengths and MO bond orders on the other side [15], linear correlations between vicinal H,H-coupling constants and bond orders might be expected. Due to the lack of reliable X-results, we used *Hammett* substituent constants σ_p^+ [11] as a measure of electronic substituents effects on bond orders and charge density.

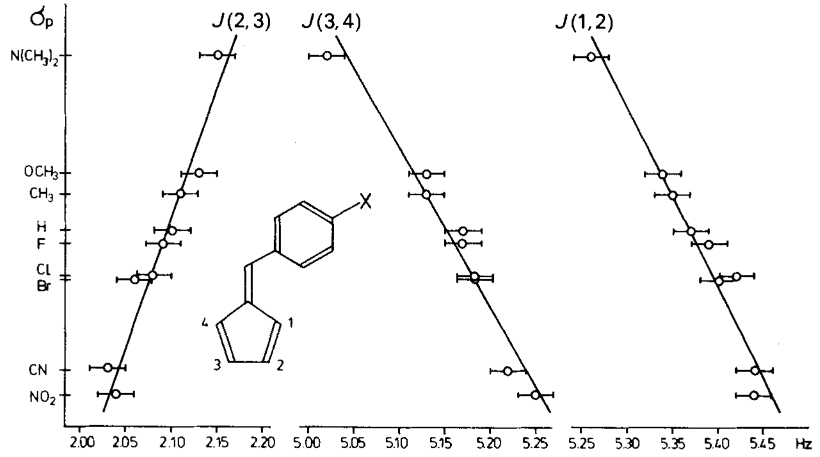


Fig. 3. *Plot of* σ_p vs. $^3J(H,H)$ *of pentafulvenes* **1**–**9**

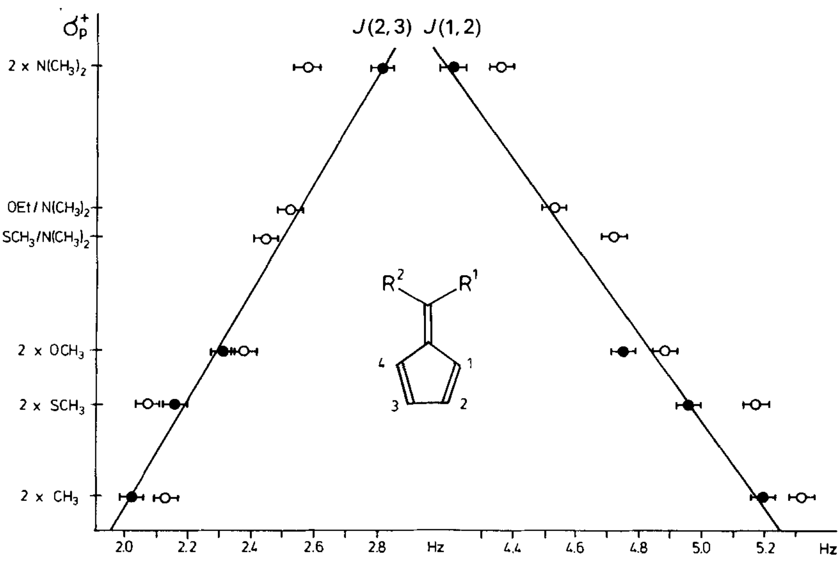


Fig. 4. *Plot of* σ_p^+ vs. $^3J(H,H)$ *of 6,6-disubstituted pentafulvenes* **13**–**22**
(●: 'bridged' pentafulvenes **20**–**23**; ○: pentafulvenes **13**–**18**)

Substituent effects on vicinal H,H-coupling constants of **1**–**9** and **13**–**23** are illustrated in *Figs. 3* and *4*. Coupling constants of both types of fulvenes show the same trends, although substituent-induced changes of ^3J-values are much larger for substituents R^1,R^2 directly bound to C(6) than for substituents X in *p*-position of the Ph ring. ***With increasing electron-donating capacity of the substituents, coupling constants** J(1,2) **and** J(3,4) **are decreasing, whereas** J(2,3) **is increasing.*** This is exactly the trend expected for an increasing π delocalisation in the 5-membered ring. Furthermore, ***linear correlations between*** ^3J***-values and*** Hammett ***substituent constants*** σ_p^+ ***are observed,*** which give good fits for 6-(*p*-X-phenyl)pentafulvenes **1–9** *(Fig. 3)* and bridged 6,6-disubstituted pentafulvenes

19–22 (*Fig. 4*, correlation coefficients 0.992 for $J(1,2) = J(3,4)$, and 0.998 for $J(2,3)$) and poorer fits for sterically different pentafulvenes **13–18**. The same trends are observed for 6-monosubstituted pentafulvenes **10–12**.

Correlations of the same type result if C–C bond lengths (*Table 5*) of bridged pentafulvenes **19–23** as obtained by MNDO calculations[2]; are plotted *vs.* the experimental ^3J coupling constants (*Fig. 5*). Correlation coefficients are 0.960 for $J(1,2)$ and 0.990 for $J(2,3)$. The same trends with poorer fits are observed for **10–18**.

Table 5. *Electron-Excess Densities* Δq_i *and C–C Bond Lengths* r_{ij} *in the Fulvene Rings of Pentafulvenes* **19–23** (MNDO)

Fulvene	Δq[a]) (C(5))	Δq[a]) (C(2)) = Δq(C(3))	Δq[a]) (C(1)) = Δq(C(4))	$r(1,2) = r(3,4)$	$r(2,3)$	$r(1,5) = r(4,5)$
19	+0.002 (+0.045, –0.043)	–0.065 (+0.007, –0.072)	–0.085 (–0.030, –0.055)	1.365	1.478	1.494
20	–0.058 (–0.018, –0.040)	–0.073 (–0.003, –0.070)	–0.078 (–0.027, –0.051)	1.366	1.475	1.493
21	–0.046 (–0.012, –0.034)	–0.069 (+0.001, –0.070)	–0.072 (–0.029, –0.043)	1.366	1.475	1.493
22	–0.144 (–0.153, +0.009)	–0.087 (–0.025, –0.062)	–0.056 (–0.028, –0.028)	1.370	1.470	1.483
23	–0.223 (–0.232, +0.009)	–0.101 (–0.045, –0.056)	–0.060 (–0.040, –0.020)	1.374	1.458	1.481

[a]) The three excess densities given have the following meaning: total excess density (π part, σ part).

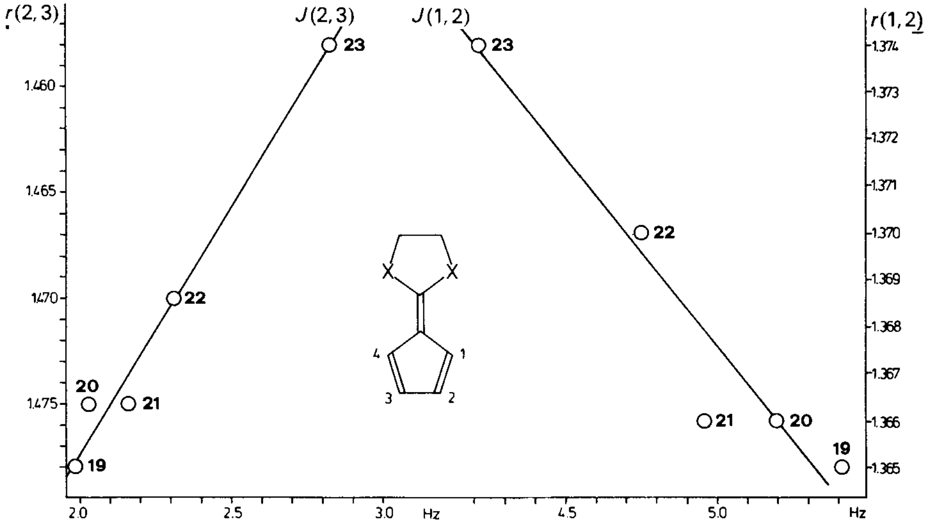


Fig. 5. *Plot of C–C bond lengths* r*(2,3) and* r*(1,2)* (in Å), *as obtained by MNDO calculations*[2]), vs. ^{3}J*(H,H) of* **19–23**[3])

These results show that substituent effects influencing bond lengths (and bond orders) may be observed in terms of relative changes of vicinal H,H-coupling constants provided that other effects are small. And that means that, in these systems, the extent of π delocalisation is qualitatively accessible from vicinal H,H-coupling constants.

5. Substituent Effects on Long-Range Coupling Constants (see *Tables 3* and *4*). – Both types of fulvenes **1–9** and **10–23** show the same trends of long-range coupling

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[2]) Details see *Exper. Part.*

[3]) $r(1,2)$ as well as $r(2,3)$ scales have been arranged so that *Fig. 5* is comparable with the *Hammett* plot of *Fig. 4*.

constants, although no linear correlations are obtained in plots of J values *vs.* substituent constants σ_p^+. According to *Table 4*, *^4J couplings* between ring protons are slightly increasing in the series **10**→**12**, **13**→**18**, and **19**→**23**, but they seem to be relatively unsensitive to changes of substituents. This result is not surprising as far as σ contributions are concerned, since any increase in π delocalisation of the 5-membered ring induces a shortening of the single bonds as well as a lengthening of the double bonds at the same time.

Small but significant changes in the opposite direction are observed for $J(2,6)$ and $J(3,6)$ which are decreasing with increasing electron-releasing capacity of X or R. Once again, this trend is reasonable, if one takes into account that the total bond length of the appropriate diene sceleton (*cf.* C(6)–C(5)–C(1)–C(2) for $^5J(2,6)$) increases from 6,6-dimethylfulvene (**13**) to 6,6-bis(dimethylamino)fulvene (**18**) according to X-ray data [13] [14].

6. Substituent Effects on ^{13}C Chemical Shifts

(see *Tables 6* and *7*). – ^{13}C Chemical shifts are an ideal probe for the investigation of charge-density effects in olefinic and aromatic molecules of similar sterical 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 [16], and good correlations of *p*- and *m*-C-atoms with appropriate *Hammett* σ constants have been obtained. For *p*-C-atoms, the best correlation is found for σ_p^+ [17].

^{13}C Chemical shifts of 6-substituted (**10**–**12**), 6,6-disubstituted (**13**–**18**), and exocyclically bridged pentafulvenes (**19**–**23**) are listed in *Table 7*. It is obvious that several effects

Table 6. *^{13}C Chemical Shifts of 6-(p-X-Phenyl)fulvenes* ($CDCl_3$, ±0.1 ppm with respect to TMS)

Compound	X	Temp. [°C]	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
1	NO_2	0	119.6	137.0	132.4	126.8	147.8	134.3	142.7	130.8	123.6	147.0
3	Br	20	119.9	135.9	131.2	127.1	145.7	136.4	135.6	131.9	131.8	123.5
8	CH_3O	20	119.8	134.8	129.7	127.4	143.2	138.2	129.5	132.4	114.2	160.5
9	$(CH_3)_2N$	25	119.3	133.4	127.8	127.4	140.5	139.6	124.5	132.6	111.7	150.9

Table 7. *^{13}C Chemical Shifts of 6-Substituted and 6,6-Disubstituted Pentafulvenes* ($CDCl_3$, ±0.1 ppm with respect to TMS)

Compound	R^1	R^2	Temp. [°C]	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3	CH_2
6	C_6H_5	H	–30	120.0	135.2	130.6	126.9	144.6	138.1		
10	$(CH_3)_3C$	H	–5	119.6	133.8	128.5	128.3	141.8	153.9	30.8	
12	$(CH_3)_2N$	H	–5	114.0	125.1	119.4	124.4	116.6	149.1	40.3, 47.1	
13	CH_3	CH_3	34	120.4	130.4	130.4	120.4	142.7	148.7	42.1	
14	CH_3S	CH_3S	–20	120.6	131.3	131.3	120.6	146.0	153.8	17.9	
15	CH_3O	CH_3O	34	118.5	122.4	122.4	118.5	102.2	164.1	57.9	
16	$(CH_3)_2N$	CH_3S	34	119.6	122.3	122.3	119.6	120.8	161.8	18.7, 43.9	
17	$(CH_3)_2N$	C_2H_5O	34	116.6	117.6	117.6	116.6	103.4	165.9	15.3, 40.2	71.7
18	$(CH_3)_2N$	$(CH_3)_2N$	34	115.8	116.8	116.8	115.8	106.4	164.5	42.0	
19	CH=CH–CH=CH[a]		–50	122.0	136.0	136.0	122.0	147.9	147.9		
20	CH_2–CH_2–CH_2–CH_2		–5	121.1	129.3	129.3	121.1	138.0	162.5		33.0,26.0
21	S–CH_2–CH_2–S		34	119.8	128.5	128.5	119.8	132.3	158.9		32.2
22	O–CH_2–CH_2–O		34	118.0	123.5	123.5	118.0	98.3	163.9		67.5
23	$N(CH_3)$–CH_2–CH_2–$N(CH_3)$		34	113.4	114.0	114.0	113.4	98.6	162.4	38.0	50.4

[a] $CDCl_3$ Soln. containing some THF.

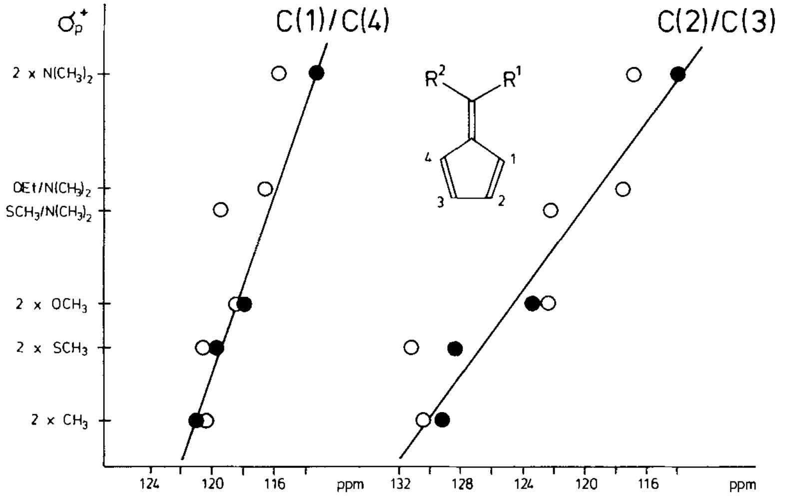

Fig. 6. *Plot of* σ_p^+ vs. *^{13}C chemical shifts* (C(1)/C(4) and C(2)/C(3)) *of 6,6-disubstituted pentafulvenes* **13–22** (●: 'bridged' pentafulvenes **20–23**; ○: pentafulvenes **13–18**)

are influencing C(6), whereas systematic substituent effects are operative on the ring C-atoms of **10–23**: electron-releasing groups at C(6) cause an overall high-field shift of the ring C-atoms which strongly decreases in the series C(5) > C(2)/C(3) > C(1)/C(4). For sterically similar pentafulvenes **19–23**, ^{13}C chemical shifts of C(2)/C(3) and C(1)/C(4) correlate surprisingly good with *Hammett* σ_p^+ constants *(Fig. 6)*. A correlation of the same type and quality (correlation coefficient of 0.967) as shown in *Fig. 6* results, if MNDO-calculated excess charges of C(2)/C(3) are plotted *vs.* ^{13}C chemical shifts. However, the same correlation for C(1)/C(4) yields the wrong sign for the slope. An independent analysis for the π and σ part of the excess electron densities *(Table 5)* shows, that

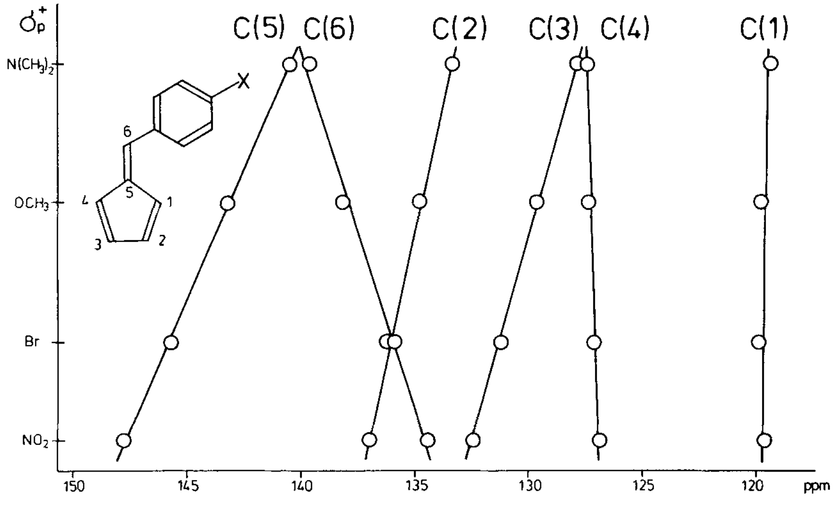

Fig. 7. *Plot of* σ_p^+ vs. *^{13}C chemical shifts of 6-(*p-*X-phenyl)pentafulvenes* **1**, **3**, **8**, *and* **9**

only the π parts give the right correlation in the C(1)/C(4) as well as the C(2)/C(3) case, whereas the slope of the correlations for the σ parts has the wrong sign in both cases. Probably, many correlations with total charge densities (*e.g.* [16]) were nevertheless successful, because usually the π part was the dominant part in these cases. As expected, **10**–**12** and **13**–**18** show the same trends, but they give rather poor correlations.

^{13}C Chemical shifts of 6-(*p*-X-phenyl)pentafulvenes **1**–**9** are listed in *Table 6*, substituent effects on fulvene C-atoms are plotted in *Fig. 7*. As we pointed out earlier [3], electron-releasing substituents X induce a high-field shift of the fulvene-ring C-atoms which strongly decreases in the series C(5) > C(2)/C(3) > C(1)/C(4). Substituent effects on C(1)/C(4) are very small and within the experimental error. That means that charge-density effects of substituents X strongly influence C(5), whereas a medium effect is felt by C(2)/C(3). With exception of C(1) (which might feel additional steric effects), good correlations are obtained for all the ring C-atoms. On the other hand, the systematic low-field shift of C(6) induced by electron-releasing substituents is quite surprising and will be discussed later.

Compared with pentafulvenes **10**–**23** (*Table 7, Fig. 6*) the overall substituent effects observed for fulvene ring C-atoms are much smaller due to the extension of the conjugative system bearing X; however, the same decrease in the series C(5) > C(2)/C(3) > C(1)/C(4) takes place. The only difference is that the effect measured for C(1)/C(4) of 6-(*p*-X-phenyl)pentafulvenes is within the experimental error, while a small but significant high-field shift of C(1)/C(4) is measured for pentafulvenes **10**–**23** bearing substituents at C(6).

7. Closing Remarks. – Systematic substituent effects have been observed in the NMR spectra of sterically similar 6,6-disubstituted pentafulvenes **19**–**23** and 6-(*p*-X-phenyl)-pentafulvenes **1**–**9** which allow conclusions concerning the extent of π delocalisation as well as charge distribution in the 5-membered ring. As expected, the effects are considerably larger for pentafulvenes bearing the substituents at C(6) than for 6-(*p*-X-phenyl)-pentafulvenes; however, the same trends are observed in the ^{1}H- and ^{13}C-NMR spectra as well. Changes of *vicinal H,H-coupling constants* with increasing electron-donating capacity of the substituent R and X are interpreted in terms of an increasing π delocalisation in the 5-membered ring. Linear correlations of *Hammett* σ_p^+ constants or MNDO-calculated C—C bond lengths and ^3J values are observed. On the other hand, a systematic high-field shift of *^{13}C chemical shifts of ring C-atoms* is induced by electron-releasing substituents R and X which decreases in the series C(5) > C(2)/C(3) > C(1)/C(4). The relative sensitivity of ring C-atoms as well as linear correlations with σ_p^+ constants suggest that a π-charge-density effect is operative.

The only surprising feature is the low-field shift of C(6) induced by electron-releasing substituents X as observed in the ^{13}C-NMR spectra of 6-(*p*-X-phenyl)fulvenes [3]. However, this shift is in full agreement with an increasingly positive excess charge on C(6). The MNDO calculation shows again, that the π part is responsible for this increase of the total excess charge. A similar but smaller substituent effect on C(6) has recently been observed by *Sardella et al.* [4] for 6-methyl-6-(*p*-X-phenyl)pentafulvenes and attributed to the operation of a 'π-polarisation effect' [18] [19].

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Experimental Part

Syntheses. – *6-(*p*-X-Phenyl)pentafulvenes* **1**–**9** have been prepared by reaction of α-chlorobenzyl acetates and α-bromobenzyl acetates [20] with cyclopentadienide [21]. A typical example is given below. All reactions have been realised in H_2O-free solvents under Ar or N_2.

*6-(*p*-Fluorophenyl)pentafulvene* (**5**). α-Chloro-*p*-fluorobenzyl acetate (6.4 g, 30 mmol) was dissolved in 30 ml of Et_2O and stirred at −30°. Within 30 min, a soln. of 40.8 mmol of sodium cyclopentadienide in THF was slowly added within the range of −25° to −30°. After stirring the orange suspension for another 30 min at −30°, 4.2 ml (30.2 mmol) of Et_3N were slowly added. The suspension was stirred for another 2 h at 0°, precipitated salts were separated by centrifugation, and solvent was removed by distillation at 10^{-2} Torr/0° to give 4.6 g of a dark-red slurry which was easily soluble in petroleum ether. The crude product was purified by column chromatography on 100 g of desactivated silica gel [21] with petroleum ether at 10°. Recrystallisation from petroleum ether: 2.8 g (54%) of red crystals of **5**, m.p. of 40–41°.

Pentafulvenes **10**–**22** have been prepared according to the indicated procedures: **10**: [21]; **11**: [22]; **12**: [23]; **13** [24]; **14**: [25]; **15**: [26]; **16**: [27]; **17**: [26]; **18**: [26]; **19**: [28]; **20**: [29]; **21**: [27]; **22**: synthesis is similar to that of **15** [26]; **23**: synthesis is similar to that of **18** [26].

NMR Spectra. – ^{1}H-NMR spectra of carefully filtered and degassed solns. of *6-monosubstituted pentafulvenes* **1**–**12** were measured at ambient temp. in $CDCl_3$ and (D_6)acetone (where highest resolution was obtained) with *Bruker WH 360* and *WH 400* spectrometers. Key proton for the assignment was H–C(2) due to its large $^5J_{ttt}$ long-range coupling with H–C(6). Analysis of the approximately first-order spectra followed by simulation and iteration gave chemical shifts and coupling constants given in *Tables 1–4*. Relative signs of coupling constants have been determined by *Philipsborn et al.* [2]. ^{1}H-NMR spectra of carefully filtered and degassed solns. of *6,6-disubstituted pentafulvenes* **13**–**18** and **20**–**23** were measured at ambient temp. in (D_6)acetone with *Bruker WP 80* (**14**–**18** and **21**–**23**), *Varian XL-100* (**13**), and *Bruker WH 360* (**20**), and analysed according to *AA'XX'* or *AA'BB'*. Simulation and iteration gave chemical shifts and coupling constants given in *Tables 2* and *4*. In most cases, assignments of pairs of protons H–C(1)/H–C(4) and H–C(2)/H–C(3) was checked by NOE by irradiating protons of substituents at C(6).

^{13}C-NMR spectra of $CDCl_3$ solns. of **1**, **3**, and **8**–**23** have been measured with *Varian XL 100* and *Bruker WH 400* spectrometers (only **1**, **3**, and **8**) in the temp. range of −50 to +34° (*cf. Tables 6* and *7*). Assignments were based on [2], they were independently checked for **1**, **3**, **8**, **9**, and **23** by selective ^{1}H,^{13}C-decoupling experiments.

MNDO Calculations. – The MNDO calculations were performed with a program obtained from QCPE [30]. All geometrical degrees of freedom were optimized, with the exception that the rings were kept planar. The selected convergency criteria together with a very flat potential prevented the establishment of a correlation between the type of substituent X and the twist angle between the rings in the Ph-substituted pentafulvenes.

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