REVIEW

Substituent Effects on π-Bond Delocalization of Fulvenes and Fulvalenes. Are Fulvenes Aromatic?

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The influence of exocyclic substituents on π-delocalization of pentafulvenes **2**, heptafulvenes **3**, and nonafulvenes **4** has been investigated.

Pentafulvenes **2**: Changes of bond lengths (induced by exocyclic substituents R^1 and R^2 of **2**) are reflected by systematic changes of $^3J(H,H)$ (*Fig. 2*) as well as of $^1J(C,C)$ coupling constants (*Fig. 4*), so that linear correlations of σ_p^+ *vs.* $^3J(H,H)$ and $^1J(C,C)$ coupling constants were obtained. Plots of that type are very useful for determining the extent of π-delocalization of various pentafulvenes **5 – 8** (*Figs. 6* and *12*). Charge density effects of pentafulvenes and pentafulvalenes were observed by substituent-induced shifts of the ring C-atoms (*Fig. 5*).

Heptafulvenes **3**: Contrary to planar pentafulvenes, heptafulvenes did not show any linear correlations of σ_p^+ *vs.* $^3J(H,H)$-plots (*Fig. 8*) or σ_p^+ *vs.* $\delta(^{13}C)$-plots (*Fig. 9*), although substituents R^1, R^2 clearly influenced $^3J(H,H)$-coupling constants as well as ^{13}C chemical shifts of the ring H-atoms and ring C-atoms. In the NMR spectra of 'heptafulvenes with inverse ring polarization' (in the lower range of *Fig. 8*), $^3J(H,H)$-coupling constants were strongly alternating and were barely influenced by exocyclic substituents. This supported a boat conformation of the corresponding heptafulvenes. In the range of *Hammett* σ_p^+-values above -0.5 to 0, strong substituent effects started to be effective, and a nearly linear approach of $^3J(H,H)$-coupling constants $J(2,3)/J(4,5)$ and $J(3,4)$ was observed. This meant that, as soon as heptafulvenes were planar or nearly planar, there existed similar substituent effects as for planar pentafulvenes. – A similar 'turning point' was observed in plots of σ_p^+ *vs.* ^{13}C-chemical shifts around $\sigma_p^+ = 0$ (*Fig. 9*): In the range of strong electron-accepting groups (above $\sigma_p^+ = 1$), there was a marked substituent-induced high-frequency shift which strongly decreased in the series $C(7) > C(2)/C(5) > C(3)/C(4)$, while $C(1)/C(6)$ was barely influenced.

Nonafulvenes **4**: Most nonafulvenes are non-planar olefins with strongly alternating vicinal H,H-coupling constants. This has been convincingly shown by the high-resolution ^1H-NMR spectrum of 10-dimethylaminononafulvene (**4c**, *Fig. 10*), which was not planar but contained a nearly planar (*E*)-dienamine substructure of the segment $C(7)=C(8)–C(9)=C(10)–NMe_2$ according to the NMR data. Only with very strong π-donors (like two dimethylamino groups in **4b**), planarization of the nine-membered ring could be observed at low temperatures (*Fig. 10*). Finally, the first stable nonatriafulvalene (11,12-bis(diethylamino)nonatriafulvalene (**10**)) existed in the planar dipolar form in the whole temperature range and even in unpolar solvents.

1. Introduction[2]). – Soon after the discovery of the first pentafulvenes by *Thiele* [2] in 1900, these molecules started to intrigue chemists. Although pentafulvenes were isomers of benzene, they showed a surprisingly high reactivity towards a variety of

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[1])   Deceased on May 7, 2015.
[2])   Parts of the introduction are identical with the introduction in [1], p. 1244 – 1245.

reagents; furthermore, they were colored and had a dipole moment. With the synthesis of the first heptafulvenes **3** [3], triafulvenes **1** [4], and nonafulvenes **4** [5] in the late 1950s and 1960s, the interest of chemists in cyclic cross-conjugated molecules was still increasing. As soon as the importance of *Hückel*'s MO treatment [6] for conjugated π-systems was recognized, numerous theoretical investigations concerning fulvenes were published. During a long period they were hampered by the fact that precise information on the parent fulvenes was missing. Furthermore, early calculations seemed to indicate that in fulvenes bond lengths were less strongly alternating than in open-chain olefinic molecules, while a simple HMO-treatment predicted a dipole moment of 4.7 D for pentafulvene (**2a**) [7], giving some importance to dipolar structures in the ground state.

This result was easily accepted by the experimental chemists, since the reactive behavior of many fulvenes was compatible with an intermediate position of fulvenes between open-chain olefinic and delocalized aromatic molecules [8]. However, with increasing refinement of HMO-methods, theoretical predictions for parent fulvenes supported molecules with strongly alternating bond lengths and a small dipole moment. For parent pentafulvene (**2a**), the calculated dipole moment dropped from 4.7 [7] to 0.45 D [9][3]), while an analysis of the microwave spectrum finally gave an experimental dipole moment of 0.424 D [11]!

Before being in the position to decide whether fulvenes were aromatic or not, or even to determine their extent of aromaticity, we first had to agree on *good criteria of aromaticity* [12]. The term 'aromatic' was first attributed to certain benzenoid derivatives owing a typical smell. Later on it was realized that the basic parent system of all these compounds was a benzene ring. So the main interest of chemists was focused on the surprising inertness of benzene to undergo reactions typical for olefinic molecules and on the strong tendency of benzene and its derivatives to undergo substitution reactions.

Since reactivity was connected to the energy difference between the ground-state of the starting material and that of the transition state, and since substituents could stabilize both states or one alone, it was dangerous to conclude from a sluggish reaction of a compound to its aromatic character. In the following, we will look for typical ground-state properties as possible criteria for aromaticity. Due to the extensive π-delocalization, benzene has been characterized by a low ground-state energy compared with appropriate open-chain molecules, such as hexa-1,3,5-triene. This energy difference[4]) ΔE_π, which is named *Dewar resonance energy* [13] has turned out to be a good aromaticity criterion for non-benzenoid cyclic conjugated compounds; however, it represented the difference between two theoretically calculated values and was dependent on the suitability of the applied model. The same was true for the *resonance energy* or *delocalization energy*, which was the energy difference between the energy calculated for the delocalized molecule minus the energy calculated for the same, but localized molecule.

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[3]) For discussions of earlier theoretical calculations and predictions see [10], pp. 168–184.

[4]) If π-systems of different ring size are compared, then resonance energies per π-electron (REPE) are normally calculated.

The extensive π-delocalization of benzene resulted in equal C–C-bond lengths (1.398 Å), in contrast to cyclohexene where the C=C bond was 1.337 Å and the adjacent C–C bonds were 1.543 Å long. So *bond length alternation* is a good qualitative criterion for deciding whether a cyclic conjugated molecule is olefinic or aromatic, provided that the data have been made available, *e.g.* from X-ray or microwave spectroscopy. There were pitfalls, however, especially if the X-ray simulated a fully delocalized structure while in fact two or more partially localized structures were rapidly interconverting.

While only a few structures of fulvenes have been determined so far by X-ray or MW-spectroscopy (see later), information on bond-length alternation was provided by NMR-spectroscopy as well. The value of vicinal H–H coupling constants ^3J(H,H) was strongly dependent on bond lengths, but unfortunately influenced by other factors as well [14], so that carefully chosen molecules had to be compared (see later). Furthermore, C–C coupling constants ^1J(C,C) were influenced by bond lengths as well, but not so easily available [14].

Highly delocalized aromatic molecules are characterized by a high mobility and easy polarizability of the π-electron cloud. In fact, *diamagnetic susceptibility* [15] may be taken as an indicator for aromaticity. However, the most well-known effect associated with delocalized aromatic π-systems is the *ring current effect* [16], by which the NMR signals of H-atoms placed in the plane and outside of the aromatic ring are strongly shifted to higher frequencies (to the left), while H-atoms within or slightly above the ring are strongly shifted to lower frequencies (to the right). Unfortunately, the ring current effect was not well suited for the investigation of aromaticity of fulvenes, because an increasing π-delocalization or aromaticity was combined with an increasing importance of dipolar structures and changes in charge density of the C-atoms, which did not only influence the ^{13}C-NMR shifts but the ^{1}H-NMR shifts as well[5]).

Finally it has to be mentioned, that *^{13}C-NMR-shifts* are very suitable for indicating changes in charge density, and it is important to note that they are not influenced by the ring current effect.

2. Aromaticity of Parent Fulvenes. – Most of the basic questions concerning parent fulvenes have been answered after their successful synthesis and spectroscopic analysis (*Table 1*). The result was that *parent fulvenes* **1a***,* **2a***,* **3a***, and* **4a** *were basically non-aromatic compounds.*

The microwave data showed that triafulvene [17], pentafulvene [11], and heptafulvene [18] were characterized by strongly alternating bond lengths and a small dipole moment. In the UV-spectrum the bathochromic shift of the longest-wavelength absorption from **1a** (309 nm) to **2a** (362 nm) and **3a** (423 nm) corresponded to the extension of the conjugative system. The dramatic hypsochromic shift of the UV-absorption of nonafulvene (255 nm) was indicative of a non-planar structure [23]. In agreement with the relatively high energy of the HOMO of fulvenes, the first ionization

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[5])   A typical example is pentafulvene (**2a**): If substituents (like NR$_2$) at the exocyclic C-atom are increasing the cyclopentadienide character of the ring, the ring current effect induces a shift to the left, while the increased negative charge density induces a shift to the right.

Table 1. *Important Spectroscopic Data*[a]) *of Parent Fulvenes* **1a – 4a**

Molecule	1a	2a	3a	4a
C–C-bond lengths (MW-spectrum)	1,2: 1.323 2,3: 1.441 3,4: 1.332 [17]	1,2: 1.355 2,3: 1.476 4,5: 1.470 5,6: 1.348 [11]	1,2: 1.365 2,3: 1.470 3,4: 1.344 6,7: 1.450 7,8: 1.350 [18]	unknown, non-planar molecule with alternating bond lengths (NMR) [19]
Dipole moment (MW)	1.90 D [17]	0.424 D [11]	0.477 D [18]	unknown
UV[b]): λ_{max} (log ε)	309 (w) [20]	362 (2.40) [21] C_6H_{12}	423 (2.68) [22] C_6H_{12}	255 (4.14) [23] C_6H_{14}
PE[c]): $I_{v.1}$ [eV]	unknown	8.55 [24]	7.69 [24]	unknown
^{1}H-NMR δ(H) [ppm]	H_1,H_2: 8.18 H_4: 3.60 CD_2Cl_2 [25]	H_1,H_4: 6.22 H_2,H_3: 6.53 H_6: 5.85 $CDCl_3$ [26]	H_1,H_6: 5.97 H_2,H_5: 5.48 H_3,H_4: 5.65 H_8: 4.45 CD_3COCD_3 [27]	H_1,H_8: 6.12 H_2,H_7: 5.63 H_3,H_6: 5.99 H_4,H_5: 5.82 H_{10}: 5.11 CD_3COCD_3 [19]
[3]J(H,H) [Hz]		$J_{1,2} = 5.10$ $J_{2,3} = 1.95$ $CDCl_3$ [26]	$J_{1,2} = 12.05$ $J_{2,3} = 7.51$ $J_{3,4} = 11.53$ CD_3COCD_3 [27]	$J_{1,2} = 12.88$ $J_{2,3} = 3.80$ $J_{3,4} = 12.16$ $J_{4,5} = 2.94$ CD_3COCD_3 [19]
^{13}C-NMR δ(C) [ppm]	C(1)/C(2): 132.9 C(4): 59.6 (D$_8$)THF [25]	C(1)/C(4): 124.9 C(2)/C(3): 134.3 C(5): 152.6 C(6): 123.4 $CDCl_3$ [26]	C(1/C(6 : 138.3 C(2)/C(5): 126.9 C(3)/C(4): 130.8 C(7): 146.6 C(8): 111.9 $CDCl_3$ [28]	C(1/C(8 : 130.4 C(2)/C(7): 127.2 C(3)/C(6): 128.7 C(4)/C(5): 126.7 C(9): 143.5 C(10): 122.0 CD_3COCD_3 [19]

[a]) For a more complete *Table* see [1]. [b]) Longest-wavelength absorption band. [c]) Lowest ionisation potential.

potential $I_{v.1}$ was small in comparison, and it decreased from pentafulvene to heptafulvene [24]. While the IR-spectra did not provide decisive information concerning the aromaticity of fulvenes, valuable conclusions could be drawn from ^{1}H- and ^{13}C-NMR spectra: The chemical shifts (δ(H)) of the H-atoms of planar pentafulvene (**2a**) and heptafulvene (**3a**) were in the olefinic region. The same was true for nonafulvene (**4a**), which deviated strongly from planarity according to UV [23] and NMR data of 10-substituted nonafulvenes [29][30][31]. On the other hand, the ^{1}H-NMR shifts of triafulvene (**1a**) were indicative of some contribution of the dipolar form **1B** (see *Fig. 1*) to the ground state: H–C(1)/H–C(2) absorbed at higher

frequencies by *ca.* 1 ppm compared with cyclopropenes, while H–C(4)/H–C(4′) absorbed at lower frequencies by *ca.* 1.4 ppm compared with its cycloaddition product, cyclopentadiene [32]. – Vicinal H,H coupling constants of the ring H-atoms were strongly alternating for pentafulvene, heptafulvene, and nonafulvene. This clearly showed that the C–C-bond lengths were strongly alternating for the planar structures of **2** and **3**, too, while for the non-planar nonafulvene **4** the ^3J(H,H) couplings over formal single bonds were additionally influenced by the dihedral angle. – Finally, ^{13}C-chemical shifts of **1a**, **2a**, and **3a** did not show considerable contributions of dipolar forms **1B**, **2B**, and **3B** (*Fig. 1*) to the ground state. Once again, the pronounced high-field position of C(4) of triafulvene (59.6 ppm) compared with its [4 + 2]-cycloaddition product with cyclopentadiene (102.2 ppm) [32] was at least partially due to some negative charge density at the exocyclic C-atom.
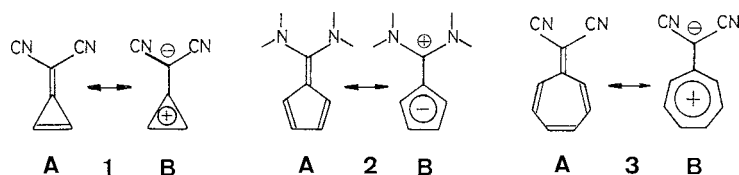
Fig. 1. *Stabilizing effects of exocyclic substituents on fulvenes*[6])

Thus, all spectroscopic results were in agreement with the basically non-aromatic character of parent fulvenes **1a** – **4a** which showed strongly alternating bond lengths and a small dipole moment and were best represented by the canonical structures **A**. A significant contribution of the dipolar structure **1B** was only felt in the ^{1}H- and especially the ^{13}C-NMR spectra of triafulvene (**1a**). NMR Data were completely compatible with the microwave data. This meant that in all cases where MW- and X-ray data were not available, NMR coupling constants and ^{13}C-chemical shifts gave a first estimate of the extent of bond-length alternation and charge distribution in these cyclic cross-conjugated molecules.

3. Influence of Substituents on the π-Delocalization of Fulvenes. – Because of the reactive behavior of some typical fulvenes, an intermediate position of fulvenes between nonbenzenoid olefinic and benzenoid aromatic molecules was assumed [8][10]. However, the spectroscopic data and the presence of small dipole moments showed, that this could certainly not be the case for parent fulvenes **1a** – **4a**. On the other hand, it was well known that triafulvenes **1** and heptafulvenes **3** were stabilized by $-M$-substituents like cyano groups, while pentafulvenes **2** were stabilized by $+M$-substituents like dimethylamino groups at the exocyclic C-atom (*Fig. 1*). Therefore, we could assume that, as far as substituent effects were concerned, two classes of fulvenes had to be distinguished: For triafulvenes (**1**) and heptafulvenes (**3**),

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[6]) As in the case of pentafulvenes (**2**), nonafulvenes (**4**) are stabilized by π-donors at the exocyclic C-atom. Because nonafulvene is not planar, $+M$-substituents induce planarization and increase π-delocalization. For non-planar nonafulvenes the canonical forms **4B** are not allowed.

electron accepting groups at the exocyclic C-atom were supposed to increase π-delocalization in the ring and separate the charges. On the other hand, for pentafulvenes (**2**) and nonafulvenes (**4**), π-delocalization and charge-separation was supposed to be enhanced by electron-donating substituents (*Fig. 1*). In the following, we will examine the influence of exocyclic substituents on bond lengths, which were directly available from X-ray and MW data and indirectly derived from NMR data.

3.1. *Triafulvenes.* Due to thermal instability, most available triafulvenes were highly substituted, so that no systematic NMR investigation was possible. Most triafulvenes were bearing phenyl groups at C(1) and C(2), as well as electron-accepting substituents at C(4). Selected structural results (concerning bond lengths) are given in *Table 2*.
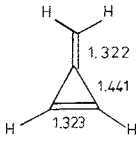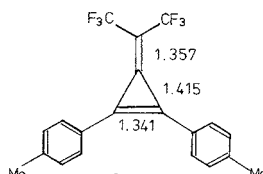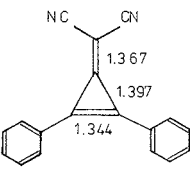
As expected from *Fig. 1*, electron-accepting groups at C(4) reduced the bond length alternations and increased the π-delocalization in the ring. While bond lengths of parent triafulvene varied considerably, all the bond lengths of 1,2-diphenyl-4,4-dicyanotriafulvene (**1c**) [34] were already of the same magnitude, and the dipole moment rose up to 7.9 D. The triafulvene derivative **1b**, one of the rare examples with strong $-I$-substituents at C(4), obviously took an intermediate position between **1a** and **1c**. It is interesting to note that the nivellation of bond lengths in the ring was mostly due to a strong decrease of formal single bonds, while the increase of the C(1)=C(2) bond was surprisingly small.

These few structural results showed that electron-accepting groups placed at the exocyclic C-atom were increasing π-delocalization and – according to the dipole moments – charge separation, too.

3.2. *Pentafulvenes.* – During the last decades of the 20th century, pentafulvenes have been thoroughly investigated[7]). It has been pointed out quite early that ^{1}H-chemical shifts were influenced by a variety of effects and did not allow conclusions concerning the aromaticity [26][35], while the size of vicinal ^{1}H,^{1}H-coupling constants qualitatively reflected the extent of bond delocalization [26][35][37]. From ^{13}C-chemical shifts it was estimated that dipolar structures (see **2B**, *Fig. 1*) to some extent contributed to the electronic ground-state of pentafulvenes [26][28][36].

In the following, we will discuss our own work concerning the influence of exocyclic substituents on the NMR parameters of pentafulvenes [38–41]. We will show that by plotting against *Hammett*-substituent constants σ or σ^+ [42] often linear correlations were observed. We started analyzing a series of 6-(*p*-X-phenyl)-pentafulvenes (**2C**),

Table 2. *MW and X-Ray Results of Triafulvene* (**1a**) *and Substituted Triafulvenes*

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had very good results with 6,6-bridged fulvenes (**2D**), medium quality results with 6-substituted, as well as 6,6-disubstituted pentafulvenes (**2E**), and found ourselves in a position to compare these results with the NMR parameters of parent pentafulvalenes **5**, **6**, and **7**, which we had synthesized before.

2C   **2D**   **2E**   n = 2 : **5**   n = 3 : **6**   n = 4 : **7**
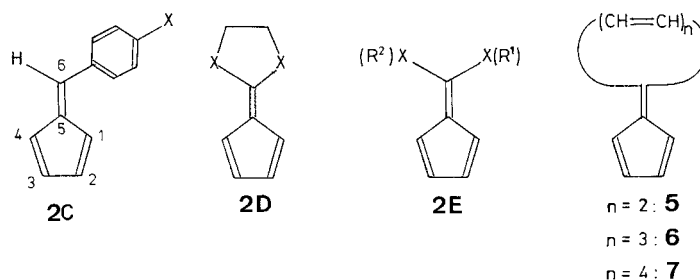
^{1}H-NMR Chemical Shifts. In all the series of pentafulvenes **2C**, **2D**, **2E**, no linear correlations between $\delta(H)$ and *Hammett*-substituent constants σ^+ had been observed, not even for the sterically least influenced (*p*-X-phenyl)pentafulvenes of type **2C**, where a certain trend could be noticed [38]. Generally, the overall effects induced by substituents on ring H-atoms were small (but the signals were scattering). This was probably due to the fact that in dipolar pentafulvenes (like 6,6-bis(dialkylamino)pentafulvenes), the charge-density effect (inducing a high-field shift) and the ring-current effect (inducing a low-field shift of the ring H-atoms) were nearly counterbalancing each other.

Vicinal H,H-Coupling Constants. It is well-known that vicinal ^{1}H,^{1}H-coupling constants were influenced by *a*) the dihedral angle, *b*) the ring size, *c*) the electronegativity of substituents, and *d*) changes in bond lengths [14]. As factors *a*) – *c*) were small or constant for the ring H-atoms of planar pentafulvenes with exocyclic substituents, the magnitude of the vicinal ^{1}H coupling constants $J(1,2)$, $J(2,3)$, and $J(3,4)$ should reflect the electronic influence of substituents on bond lengths of the fulvene ring. So far, only a few X-ray structures of pentafulvenes have been determined, but they showed that, moving from 6,6-dimethylpentafulvene [43] to 6,6-bis(dimethylamino)pentafulvene [44], the bond lengths of formal C=C bonds increased, while the bond lengths of formal C–C bonds got shorter. Considering the linear relationship between bond lengths and ^3J(H,H)-values on one side [14] and between bond lengths and MO-bond orders on the other side for benzenoid compounds [45], similar correlations could exist for pentafulvenes, too.

Substituent effects on vicinal ^{1}H,^{1}H-coupling constants of 6,6-disubstituted pentafulvenes **2**[8]) are plotted against *Hammett*-substituent constants σ_p^+ as depicted in *Fig. 2*. With increasing electron-donating quality of the substituents, $J(1,2)$ and $J(3,4)$ were decreasing, while $J(2,3)$ was increasing. This was the trend which was expected for

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[8]) 6-(*p*-X-Phenyl)pentafulvenes (see series **2C**) showed the same substituent effects with good correlations, but considerably smaller, as expected.

an increasing π-delocalization in a five membered ring. Furthermore, exocyclically bridged pentafulvenes showed excellent correlations, while non-bridged 6,6-disubstituted pentafulvenes showed the same trends with more scattering. According to *Fig. 3*, correlations of similar quality were obtained when ^3J(H,H) coupling constants of bridged pentafulvenes were plotted against MNDO-calculated bond lengths.

These results showed that exocyclic substituents do influence bond lengths of pentafulvenes, so that the extent of π-delocalization is accessible *via* ^{1}H,^{1}H coupling constants provided that other effects are small. And the good correlations of exocyclically bridged pentafulvenes showed that in pentafulvenes the extent of π-delocalization was accessible from ^{3}J(H,H) coupling constants!

$^{13}C,^{13}C$ Coupling Constants ^{1}J(C,C). Substituent-induced changes of bond lengths could result in changes of ^{13}C,^{13}C-NMR coupling constants as well, however these values were not so easily accessible due to the small concentration of isotopomers with two adjacent ^{13}C-atoms in the fulvene molecule.

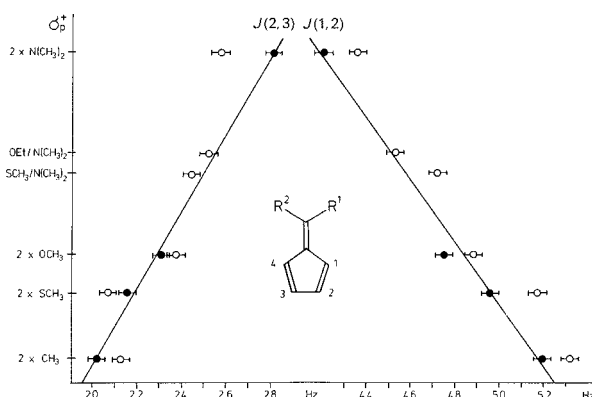Fig. 2. *Influence of substituents on ^{3}J(H,H)-coupling constants of 6,6-disubstituted pentafulvenes* (●: bridged; ○: not-bridged pentafulvenes)

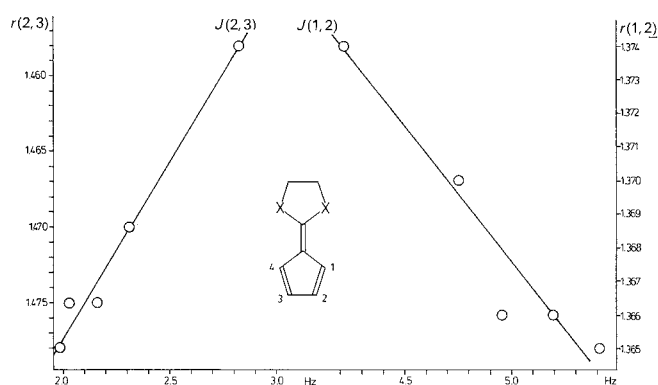Fig. 3. *MNDO-Calculated bond lengths plotted against ^{3}J(H,H) coupling constants of bridged pentafulvenes*

^{13}C-NMR Spectra investigations of benzenoid aromatic compounds indicated that [1]J(C,C)-coupling constants were increasing with decreasing bond lengths [46], but these correlations were not satisfactory enough [14], as different ring systems were compared.

[13]C,[13]C Coupling constants of a series of monosubstituted pentafulvenes have been determined by INADEQUATE pulse sequences [47] and were plotted against σ_p^+ [40] (*Fig. 4*). For unpolar pentafulvenes, [1]J(C,C)-values were strongly alternating: Coupling constants over formal C=C bonds were relatively large (65 – 69 Hz), while couplings over formal C–C bonds were relatively small (48 – 50.5 Hz). It's important to note that the [1]J(C,C) values were influenced by substituents at C(6): With increasing electron-donating character of the substituent at C(6), the values of $J(1,2)$ as well as $J(3,4)$ were decreasing, while couplings over formal C–C bonds were significantly increasing. Plotting the coupling constants against *Hammett*-substituent constants (*Fig. 4*) gave good correlations[9]) [40].

The important result was that [1]J(C,C) coupling constants of the ring-C-atoms of pentafulvenes showed the same type of influence as [3]J(H,H) coupling constants. In the plots of *Fig. 4*, there was not much difference between $J(1,2)$ and $J(3,4)$. The same was true for $J(1,5)$ and $J(4,5)$, but both coupling constants were larger than $J(2,3)$ by *ca.* 2 Hz. The cause for that difference could have resulted from the different geometry of C(5), and therefore we concluded that $J(2,3)$ was more reliable for making any conclusions on the π-delocalization. Extrapolation of the averaged slopes of $J(1,2)$/ $J(3,4)$ and that of $J(2,3)$ to the intersection, and projection on the abscissa gave a value of 56.4 Hz for a complete π-delocalization, which fitted well to the [1]J(C,C) coupling constant of 56.0 Hz for fully delocalized benzene.

[13]C Chemical Shifts. ^{13}C-NMR shifts are very useful for the investigation of charge density effects in olefinic and aromatic compounds with sterically similar environment.
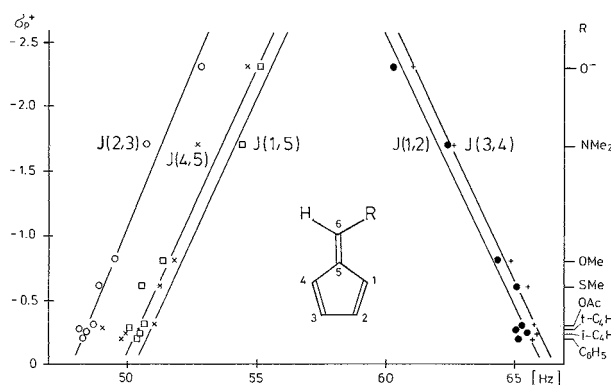

Fig. 4. *Influence of substituents on [1]J(C,C)-coupling constants of 6-substituted pentafulvenes*

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[9]) Correlation coefficients (eight pentafulvenes): $J(1,2) = 0.985$; $J(2,3) = 0.984$; $J(3,4) = 0.990$; $J(4,5) = 0.939$; $J(1,5) = 0.975$. They were even better than those of the corresponding [3]J(H,H) coupling constants of the same eight pentafulvenes: $J(1,2) = 0.956$; $J(2,3) = 0.964$; and $J(3,4) = 0.870$ [40].

For monosubstituted benzenes, ^{13}C chemical shifts of the *p*-C-atoms correlated well with the charge densities calculated by CNDO/2 [48], and for *p*- and *m*-C-atoms, good correlations with *Hammett*-substituent constants σ were obtained [49].

^{13}C-NMR shifts of 6,6-disubstituted pentafulvenes were plotted against *Hammett*-substituent constants σ_p^+ in *Fig. 4* and summarized in *Table 3*. With increasing electron-donating capacity of the exocyclic substituents, a high-field shift of the ring-C-atoms was observed, which decreased in the series $C(5)^{10)} > C(2,3) > C(1,4)$. For the exocyclically bridged (sterically similar) pentafulvenes [●], good correlations with *Hammett* σ_p^+-constants were found. Open-chain pentafulvenes [○] showed the same trends with more scattering. The same results were observed for 6-substituted pentafulvenes, as well as for 6-(*p*-X-phenyl)pentafulvenes [38][39]. They showed that charge-density effects are seen in ^{13}C-NMR spectra of pentafulvenes$^{11)}$!

3.3. *^{3}J(H,H) Coupling Constants as a Simple Aromaticity Criterion for Pentaful-venes and Pentafulvalenes.* *Fig. 2* showed that vicinal ^{1}H,^{1}H-coupling constants $J(1,2)$ and $J(2,3)$ of pentafulvenes **2** were approaching with an increasing π-donor effect of the substituents at C(6). Obviously, the approach of coupling constants was due to an increasing π-delocalization in the five-membered ring which resulted in an increase of formal C=C-bond lengths and a decrease of formal C–C-bond lengths (*Fig. 5*).

Table 3. *^{3}J(H,H)-Coupling Constants and ^{13}C Chemical Shifts of Exocyclically Bridged Pentafulvenes of Type* **2D** *as well as of Pentafulvalenes* **5**, **6**, *and* **7**
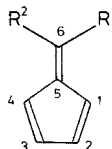
R^1,R^2	$J(1,2)$	$J(2,3)$	$C(1,4)$	$C(2,3)$	$C(5)$
(CH=CH)$_2$	5.41^a)	1.99	122.0^b)	136.0	147.9
(CH=CH)$_4$	5.32^c)	2.12	121.1^c)	132.1	143.0
(CH$_2$)$_4$	5.19^c)	2.03	121.1^b)	129.3	138.0
(CH=CH)$_3$	5.2^d)	2.2	118.6^b)	129.6	138.6
S(CH$_2$)$_2$S	4.95^c)	2.16	119.8^b)	128.5	132.3
O(CH$_2$)$_2$O	4.75^c)	2.31	118.0^b)	123.5	98.3
MeN(CH$_2$)$_2$NMe	4.21^c)	2.82	113.4^b)	114.0	98.6

^{a}) CD$_2$Cl$_2$. ^{b}) CDCl$_3$. ^{c}) (D$_6$)Acetone. ^{d}) (D$_6$)Benzene.

$^{10)}$ For more chemical shifts of C(5), see *Table 3*. C(5) is under the strongest influence of π-donors, but, because of steric influences, correlations are not good. The difference $\Delta\delta$ from the top- and the bottom-values of *Table 3* decrease in the series from C(5) ($\Delta\delta = 49.3$ ppm) to C(2,3) ($\Delta\delta = 22$ ppm) and C(1,4) ($\Delta\delta = 8.6$ ppm).

$^{11)}$ Good correlations of the same quality as in *Fig. 5* were obtained, if MNDO-calculated excess charges were plotted against ^{13}C-NMR shifts. However, the same plot for C(1,4) gave a wrong inclination for the slope. An independent analysis for the π- and σ-part of the excess-charge density showed that only the π-part gave the right correlation [39][50].
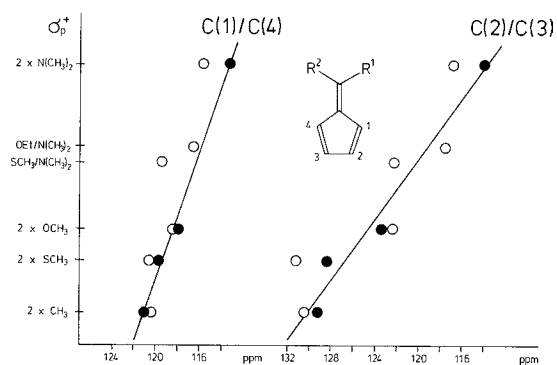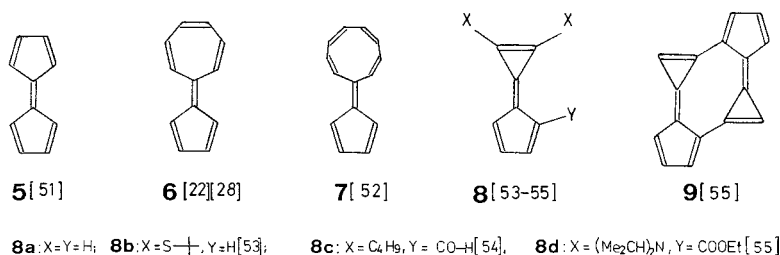
Fig. 5. *Influence of substituents on ^{13}C-NMR shifts of 6,6-disubstituted pentafulvenes (●: bridged; ○: not-bridged pentafulvenes)*

It would be interesting to test the reliability of such correlation diagrams by entering pairs of coupling constants of parent pentafulvalenes **5**, **6**, and **7**, where only small changes in π-delocalization (as well as charge density) in the five membered ring have to be expected. For instance, changing from pentafulvene (**2a**) to pentafulvalene (**5**), the new diene bridge of **5** is expected to be a weak π-acceptor, reducing the small dipole moment (0.424 D) of **2a** to zero. On the other hand, the new triene bridge of sequifulvalene (**6**) is expected to act as a weak π-donor (which is supported by the dipole moment of **6** ($\mu = 2.2$ D).

5[51]   **6** [22][28]   **7**[52]   **8**[53–55]   **9**[55]

8a:X=Y=H; **8b**:X=S—⊥,Y=H[53];   **8c**: X = C$_4$H$_9$, Y = CO–H[54],   **8d**: X = (Me$_2$CH)$_2$N, Y = COOEt[55]

One serious problem concerning plotting of pairs of coupling constants of pentafulvalenes against σ_p^+ was the fact that *Hammett*-substituent constants of the diene, triene, and tetraene bridges of **5**, **6**, and **7** were not known. Therefore, a modified procedure had to be adopted which made use of the pentafulvene plot (black slopes in *Fig. 6*). For each compound, the set of coupling constants $J(1,2)/J(2,3)$ was entered into *Fig. 6*, and the intersections with the two slopes of the pentafulvene plot were marked. Since there was only one correct (but unknown) σ_p^+ value for each bridge, the pair of intersections of each compound had to be averaged to the best horizontal line giving the black circles [●] in *Fig. 6*. These circles were slightly next to the pentafulvene slopes, but showed the right sequence (see above) and the same trend as the pentafulvene plots[12]).

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[12]   At the moment, this argumentation is not very convincing since the three pairs of dots [●] are very close together in *Fig. 6*. It will get much stronger by entering a set of calicenes **8**, as well as **9** into the plot (see text and *Fig. 7*).
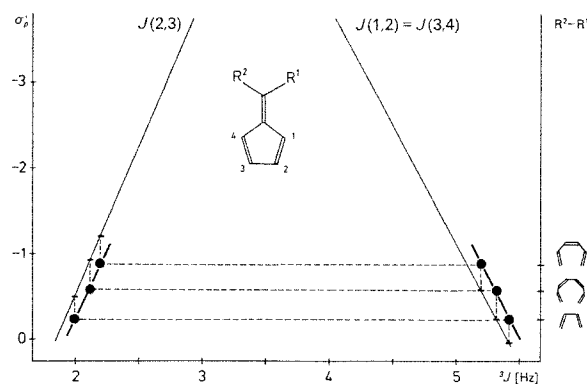
Fig. 6. *Entering* ^{3}J*(H,H)-couplings of* **5**, **6**, *and* **7** *into the pentafulvene plot*

For completing the series of pentafulvalenes, the pentatriafulvalene (= calicene **8a**, X = Y = H) was needed, because the electron-releasing power of the C=C-bridge was assumed to be stronger than that of the triene unit of sesquifulvalene (**6**)[13]. Unfortunately, calicene **8a** is still unknown, and there are only a few known calicenes having at least three vicinal H-atoms in the ring. – In *Fig. 7* sets of coupling constants of calicenes (**8b** – **8d**) [53 – 55] were entered in the plot of *Fig. 6*. The nearly perfect fit of the three new sets of ^{3}J(H,H)-values to the new 'pentafulvalene plot' (bold lines) allowed to mark the intersection of the two slopes giving $J(1,2) = J(2,3) = 3.65$ Hz for a complete π-delocalization in the five-membered ring of pentafulvalenes. This value
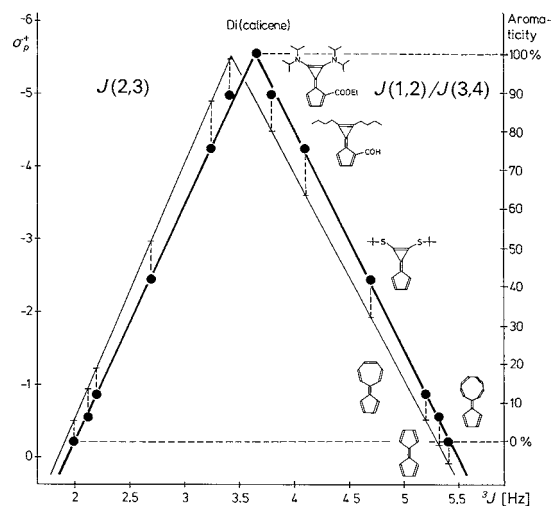

Fig. 7. *Pentafulvene plot* (thin lines) *as well as pentafulvalene plot* (bold lines)

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[13]) This is seen by analogy: the dipole moment of triafulvene (**1a**; $\mu = 1.90$ D [17]) was considerably larger than that of heptafulvene (**3a**) ($\mu = 0.477$ D [18]), while both rings were positively polarized.

matched the experimental result of $J(1,2) = J(2,3) = 3.65$ Hz of 'dicalicene' **9** which seemed to be fully delocalized according to X-ray data [55][14]).

Diagrams like *Fig. 7* might be very useful for estimating the extent of π-delocalization (or aromaticity) of pentafulvenes (thin lines) and pentafulvalenes (bold lines) from $^3J(H,H)$ values. Obviously, the intersection of the lines of each slope marked the equal coupling constants $J(1,2) = J(2,3)$; it corresponded to a completely delocalized π-system or to a compound which is 100% aromatic. It is not clear which set of ^3J-coupling constants would correspond to a localized pentafulvene with an aromaticity of 0%. Clearly, pentafulvalene (**5**) has the highest localized π-system of all the compounds given in *Fig. 7* and *Table 3*, and the contribution of the dipolar form **B** (see *Fig. 1*) to the ground-state is reduced to zero[15]). Because of that it is reasonable to take the experimental set of ^3J-values of pentafulvalene for marking a 0% aromaticity in *Fig. 7*. – This leads to an **aromaticity scale for pentafulvenes and pentafulvalenes** which is given on the right side of *Fig. 7*.

Finally one could ask whether the difference between the slopes of pentafulvenes and pentafulvalenes (*Fig. 7*) was significant or within the range of normal scattering. According to *Fig. 7*, ^3J-values of pentafulvenes were slightly smaller by *ca.* 0.15 Hz compared with pentafulvalenes of the same σ_p^+. Since correlations of σ_p^+ *vs.* ^3J were good for pentafulvenes and excellent for pentafulvalenes, the difference could be systematic[16]).

3.4. *Heptafulvenes.* Heptafulvenes **3** showed the same polarization as triafulvenes did. According to *Fig. 1*, π-delocalization as well as charge separation should be enhanced by electron-accepting substituents at C(8). Structural problems were complicated by the fact that – in contrast to planar heptafulvene [18], a lot of 8.8-disubstituted heptafulvenes were predicted [57] and experimentally found to assume a boat conformation with varying structural angles α and β. This was in particular true for heptafulvenes with electron-donating substituents at C(8) ('heptafulvenes with inverse electron demand') [58][59]. After 1970, a lot of heptafulvenes with substituents at C(8) had been synthesized. Parent heptafulvene (**3a**) has been fully characterized spectroscopically [18][22], and the X-ray data of several heptafulvenes are known (*Table 4*).

The results summarized in *Table 4* showed that heptafulvenes with π-donor groups at C(8) were not planar and prefered the boat conformation. According to microwave results [18], parent heptafulvene (**3a**) existed in a planar equilibrium structure, while heptafulvenes with strong π-acceptors at C(8) were planar or nearly planar, as well as the seven-membered ring of tropylium salts. For heptafulvenes with strong π-acceptors at C(8) planarization was accompanied by approaching C–C and C=C bonds.

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[14])   According to X-ray data [55], dicalicene (**9**) is fully delocalized. However, equal bond lengths in **9** could be faked by a very rapid valence isomerization [56], which in **9** consists in a rapid change between two pairs of calicene subunits (in formula **9** the two vertically arranged calicene subunits have been drawn).

[15])   Note that, according to the canonical structures **2A** ↔ **2B**, an increasing dipolar character of pentafulvenes is associated with an increasing π-delocalization in the ring! By symmetry, the dipole moment for **5** is $\mu = 0$.

[16])   For more discussions, see [41].

Table 4. *X-ray Data of Selected Heptafulvenes* (**3**)[a]
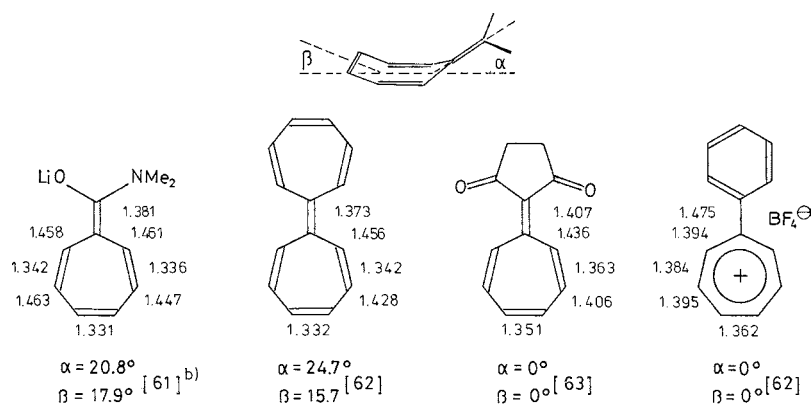
[a]) 8,8-Dicyanoheptafulvene is practically planar: $\alpha = 2.6°$, $\beta = 1.8°$ [60]. [b]) Complex of 2 Li-heptafulvenolates $\times$ 4 THF. The second heptafulvenolate molecule has very similar bond lengths, but $\alpha = 14.8°$ and $\beta = 12.6°$. For more data, see [61].

In *Fig. 8*, as well as in *Fig. 9*, the most important results of our systematic NMR investigation of some well-known and of some new [63] heptafulvenes were summarized [27][64].

Substituent Effects on ^{3}J*(H,H) Coupling Constants* (*Fig. 8*). In the ^{1}H-NMR spectra of 'heptafulvenes with inverse ring polarization' (in the lower part of *Fig. 8*), ^{3}J(H,H)-coupling constants J(2,3)/J(4,5) as well as J(3,4) were strongly alternating and were barely influenced by exocyclic substituents. This finding supported the boat conformation of the corresponding heptafulvenes. In the range of *Hammett* σ^+-values around -0.5 to 0, strong substituent effects started to be effective, and we observed a nearly linear approach of coupling constants in the range of medium to strong π-acceptors (in the upper part of *Fig. 8*). This meant that, as soon as the heptafulvene was
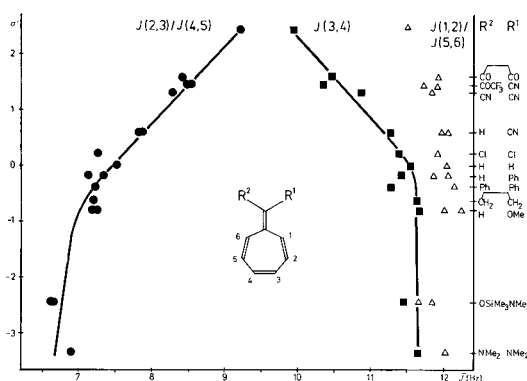
Fig. 8. *Influence of substituents on* ^{3}J*(H,H)-coupling constants of heptafulvenes* (**3**)

planar or nearly planar, we had similar substituent effects as for the planar pentafulvenes. The surprising result was however, that the sets of $J(1,2)/J(5,6)$, which were supposed to behave similarly to $J(3,4)$, nearly didn't change in the whole range[17])!

Substituent Effects on ^{13}C *Chemical Shifts* (*Fig. 9*). In the ^{13}C-NMR spectra[18]), we observed good correlations for the substituent-induced changes of C(2)/C(5) and C(3)/C(4), while, as expected, C(7) was scattering, because steric effects were strongly felt[19]). Once again we had two ranges with different slopes of the segments, a 'turning range' around $\sigma^+ = 0$ and strong linear substituent effects above $\sigma^+ = 1$, in the area of strong electron-accepting groups. *Fig. 9* shows that the substituent-induced high-frequency shift (to higher ppm-values) strongly decreased in the series C(7) > C(2)/C(5) > C(3)/C(4), while C(1)/C(6) were scattering around 136 ppm (*Table 5*). This was reasonable, since MNDO calculations predicted a very small substituent-induced excess charge for C(1)/C(6). *Table 5* shows that the maximum high-frequency shift $\Delta\delta_{max}$ strongly decayed in the series C(7): 58.0 > C(2)/C(5): 17.8C(3)/C(4): 9.8 > C(1)/C(6): − 4.0.

In summary, $^3J(H,H)$ coupling constants (*Fig. 8*), as well as ^{13}C chemical shifts (*Fig. 9*) of heptafulvenes clearly showed the conformational changes of heptafulvenes, but some questions still remained to be open [63].

3.5. *Nonafulvenes*. Planar nonafulvenes **4** are expected to exhibit the same π-polarization like pentafulvenes **2**. As shown in *Fig. 1* for pentafulvenes, π-delocalization, as well as charge separation, should be enhanced by electron-donating substituents at the exocyclic C-atom. Structural problems were additionaly complicated by
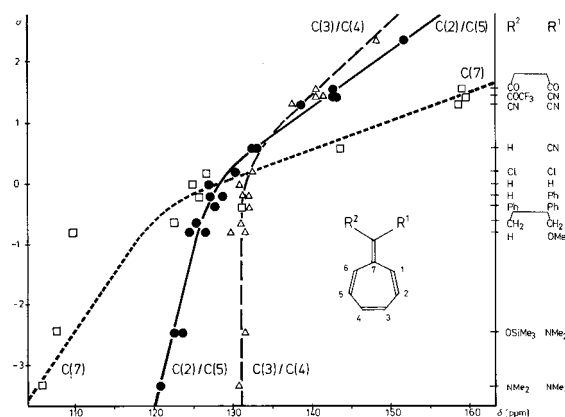

Fig. 9. *Influence of substituents on* ^{13}C-*NMR chemical shifts of heptafulvenes* (**3**)

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17) For a more detailed discussion of this problem, see [63].

18) Note that in *Fig. 9* ppm numbers increased from the left to the right, contrary to normal NMR spectra.

19) As *Table 5* shows, C(1)/C(6) were basically not influenced by substituents and were scattering around 136 ± 5 ppm. In contrast to ^3J coupling constants $J(1,2)/J(5,6)$, this behavior can be reasonably explained!
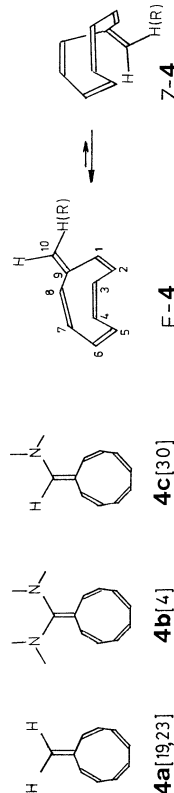
Table 5. *NMR Results of Selected Heptafulvenes* (**3**)

R¹	R²	J(1,2)/J(5,6)	J(2,3)/J(4,5)	J(3,4)	C(7)	C(2)/C(5)	C(3)/C(4)	C(1)/C(6)	C(8)
NMe₂	NMe₂[a]	12.03	6.92	11.63	105.70	120.80	130.80	139.30	157.50
	(CH₂)₄ [b]	?	7.20	11.62	129.67	125.36	131.00	135.86	139.73
Ph	Ph[a]	12.13	7.21	11.28	136.61	127.48	132.00	135.71	135.62
H	H[a]	12.05	7.51	11.53	146.6[c]	126.90	130.80	138.30	111.90[c]
Cl	Cl[b]	11.91	7.24	11.93	135.54	130.15	132.35	130.62	113.15
	COCH₂CH₂CO[a]	11.91	8.39	10.45	158.94	142.93	140.60	139.02	114.52
CN	CN[a]	11.82	8.27	10.88	163.70	138.65	137.42	135.30	70.10
¹³C : Δδ_max (ppm)				58.0	17.85	9.8	−4.0		

[a]) ¹H-NMR: (D₆)acetone, ¹³C-NMR: CDCl₃. [b]) ¹H- and ¹³C-NMR: (D₆)acetone. [c]) Value is not comparable, because **3a** has no substituents at C(8).

Table 6. *Nonafulvenes* (**4**) *with Typical ¹H-NMR Spectra, Conformational Equilibrium and H,H-Coupling Constants of 10-Dimethylaminononafulvene* (**4c**)

4a[19,23]　　**4b**[4]　　**4c**[30]

E-**4**　⇌　Z-**4**

³J couplings (**4c**)		⁴J couplings (**4c**)		⁵J couplings (**4c**)		⁶J couplings (**4c**)
J(1,2) = 12.00	J(5,6) = 12.28	J(1,3) = 1.63	J(4,6) = 0.97	J(1,4) = 0.31	J(3,6) = 0.40	J(1,6) = 0.15
J(2,3) = 2.73	J(6,7) = 5.27	J(1,8) = 0.38	J(5,7) = 1.36	J(1,7) = 0.43	J(4,7) = 2.03	J(4,8) = 0.38
J(3,4) = 11.82	J(7,8) = 13.05	J(1,10) = 1.29	J(6,8) = 0.88	J(2,5) = 2.21	J(5,8) = 0.82	J(6,10) = 0.44
J(4,5) = 3.03	J(2,4) = 1.62	J(8,10) = 0.84	J(2,10) = 0.83	J(7,10) = 0.46		
		J(3,5) = 1.20				

the fact that non-polar nonafulvenes were experimentally found to be non-planar. This was easily derived from the longest-wavelength absorption of the parent nonafulvene (**4a**; $\lambda_{max} = 255$ nm) compared with pentafulvene (**2a**; $\lambda_{max} = 362$ nm) and heptafulvene (**3a**; $\lambda_{max} = 423$ nm). On the other hand, pairs of ring H-atoms and of ring C-atoms of parent **4a** were equivalent, which hinted at an easy switch of the exocyclic C=C bond, by which diastereoisotopic ring segments were transformed into each other (see *Formula* in *Table 6*). These early conclusions [23] have been confirmed later on by extensive NMR-investigations of parent **4a** [19] as well as of new nonafulvenes [31][65]. Until 2000, no X-ray data of nonafulvenes were known.

For quite a long time, NMR-analysis of nonafulvene spectra was hampered by relatively badly resolved high-order spectra. An important breakthrough was realized with high-resolution ¹H-NMR spectrum of 10-dimethylaminononafulvene (**4c**) at 400 MHz (*Fig. 10*), whose complete analysis [29] gave all the $^3J(H,H)$-couplings as well as 20 long-range couplings (*Table 6*) [30]. *Fig. 10* demonstrates the excellent fit of the experimental and the calculated spectra. All the signals are in the olefinic range, and there are no changes with solvent polarity or temperature. Consequently, 10-dimethylaminononafulvene (**4c**) is an *olefinic molecule*.

There was an extreme alternation of vicinal ¹H,¹H-coupling constants of **4c** (*Table 6*). While ^3J coupling constants over formal C=C bonds were large, ^3J coupling constants over formal C–C bonds were surprisingly small, showing the influence of bond lengths *and* dihedral angle and confirming the nonplanar geometry of the ring. Furthermore, the analysis showed that the (*E*)-dienamine substructure C(7)=C(8)–C(9)=C(10)–NMe₂ was nearly planar (look at (*E*)-**4** in *Table 6*).

While for **4c** the conformation (*E*)-**4c** was favored, 1:1 equilibria of the type (*E*)-**4** → (*Z*)-**4** were expected and found for substituted nonafulvenes bearing two identical groups at C(10) which lead to averaged signals and coupling constants of pairs of ring H-atoms.

With one exception, all the nonafulvenes prepared so far did not show any dependence of ¹H or ¹³C chemical shifts or coupling constants on temperature or solvent polarity. The exception is 10,10-bis(dimethylamino)nonafulvene (**4b**) [5], whose surprising NMR-spectroscopic behavior has been observed for the first time by
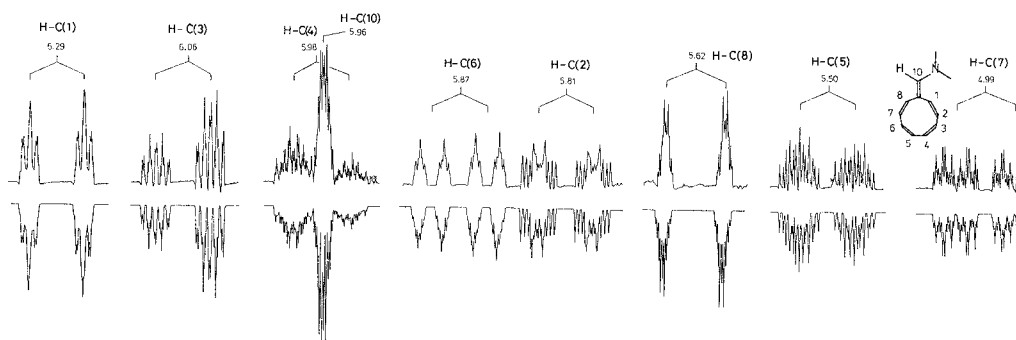

Fig. 10. *High-resolution ¹H-NMR spectrum of 10-dimethylaminononafulvene* (**4c**) (400 MHz, CD₂Cl₂, $-10°$). Upper trace: *experimental spectrum*; lower trace: *calculated spectrum with the final set of δ- and* J-*values*.
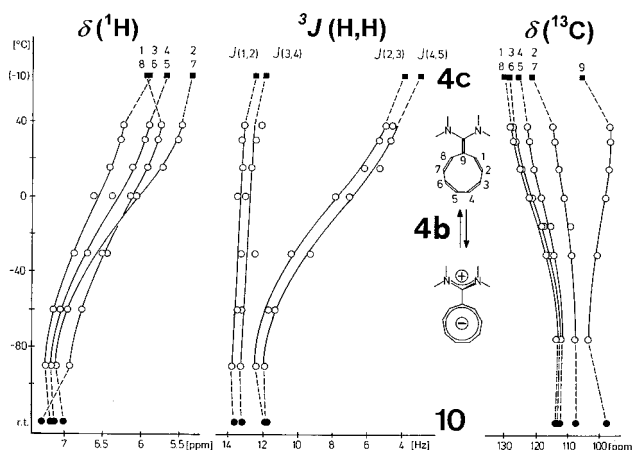
Fig. 11. top (■): *NMR-parameters of* **4c** ((D$_6$)acetone, $-10°$); middle (○): *temperature-dependent NMR parameters of* **4b** (CD$_2$Cl$_2$, $+38°$ to $-85°$); bottom (●): *NMR-parameters of* **10** (CDCl$_3$, 20°).

Hafner and *Tappe* [5][20]), explained by *Boche* [67][21]) and confirmed by our NMR-investigations (see *Fig. 11* [69][70]).

At 40° and in unpolar solvents, the ^{1}H-NMR signals of **4b** absorbed in the olefinic range (very similar to **4c** (*Fig. 11*, top)), and the vicinal coupling constants were strongly alternating. By lowering the temperature to $-85°$, the ^{1}H-NMR signals shifted to the left into the aromatic range, ^3J(H,H) couplings were approaching and the ^{13}C-NMR signals of the ring-C-atoms C(1)–C(8) experienced a high-field shift[22]).

In analogy to nonafulvenolates [67], this behavior was in agreement with a temperature-dependent equilibrium between a non-planar olefinic nonafulvene **4b** and a planar dipolar formamidinium-cyclononatetraenide **4b**$^\pm$ (*Scheme 1*): Around room temperature and in unpolar solvents the olefine **4b** was favored, while at low temperatures and/or in polar solvents the cyclononatetraenide **4b**$^\pm$ dominated.

Scheme 1

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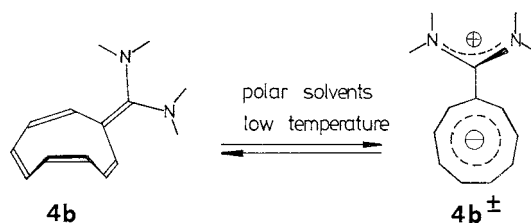
[20])　Originally, *Hafner* [66] explained the surprising temperature dependence of the ^{1}H-NMR spectra of **4b** with a 4π-valence isomerization of the nine-membered ring of **4b**.

[21])　By acylation of cyclononatetraenide, *Boche* [67] prepared a series of nonafulvenolates which could react to give 10-heterosubstituted nonafulvenes [68]. Several nonafulvenolates showed a temperature dependence similar to **4b**.

[22])　C(9) is influenced by steric effects as well.

We were concluding our work in the nonafulvene area with the synthesis of the first nonatriafulvalene **10** (*Scheme 2*) [69], in which the nonafulvene unit was connected with a cyclopropene unit (a π-donor), which by itself bears two dialkylamino groups as strong π-donors. The NMR parameters of **10** are given in *Fig. 11* (bottom, ●). At room temperature the ^{1}H-NMR signals were in the aromatic range, all ^3J couplings were large, and the ^{13}C-NMR signals of the nine-membered ring were at high field. The spectra didn't change in the whole temperature range of *Fig. 11* or with solvent polarity, and all the NMR parameters were nearly identical with the low-temperature spectra of **4b**$^\pm$ (see *Fig. 11*). That meant that the nonatriafulvalene **10** showed all the properties of a cyclopropenylium-cyclononatetraenide **10**$^\pm$ [70]!

Scheme 2. *Synthesis of an 'Aromatic' Nonafulvene* **10**$^{\pm\,23}$)
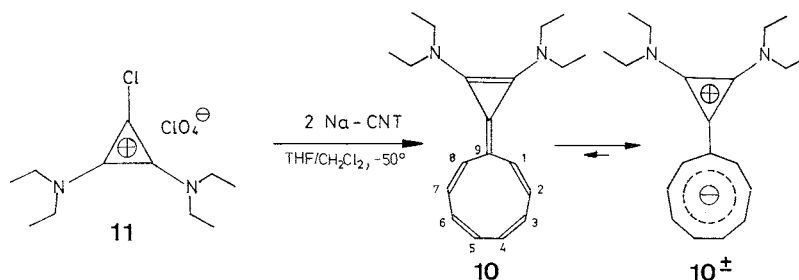
4. Summary. – X-Ray analysis and spectroscopic investigations showed that the parent fulvenes triafulvene (**1a**), pentafulvene (**2a**), heptafulvene (**3a**), and nonafulvene (**4a**) were typical olefins, which were characterized by alternating bond lengths and a small dipole moment.

Fulvenes can be divided into two classes: Triafulvenes (**1**) and heptafulvenes (**3**) were stabilized by electron-accepting substituents at the exocyclic C-atom. An increasing $-M$-effect of the substituents reduced bond-length alternation and increased π-delocalization in the ring. At the same time, the seven-membered ring of heptafulvenes was planarized.

On the other hand, pentafulvenes (**2**) and nonafulvenes (**4**) were stabilized by electron-donors at the exocyclic C-atom. The effects were easily observed for planar pentafulvenes, where the result of an increased π-delocalization was an approach of ^3J(H,H)-coupling constants. Plotting ^3J(H,H)-coupling constants against *Hammett*-substituent constants gave linear plots (*Fig. 12*), from which the extent of π-delocalization or aromaticity could be derived.

Most nonafulvenes **4** are non-planar olefins with strongly alternating vicinal coupling constants. Only with very strong π-donors, planarization of the nine-membered ring could be observed. The first stable nonatriafulvalene **10** (11,12-bis(diethylamino)nonatriafulvalene) has been synthesized, which existed in the whole temperature range in the dipolar form **10**$^\pm$.

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^{23})　The synthesis of **10** has been attempted before [53], but resulted in a valence isomerization product.
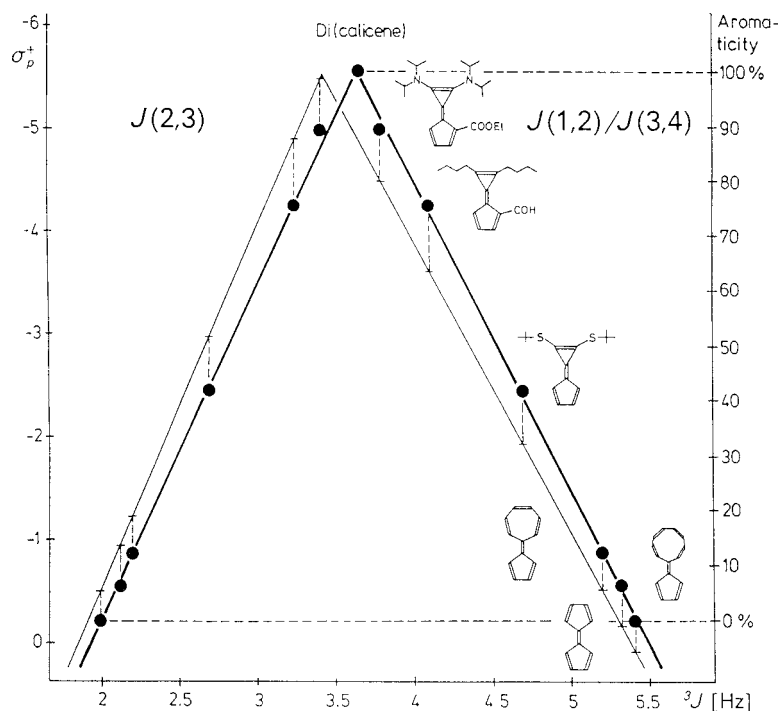
Fig. 12. *Influence of substituents on* ^{3}J(H,H) *coupling constants of pentafulvenes* (**2**) *and pentafulvalenes: Hammett* plots for deriving the extent of 'aromaticity'

Our investigations showed that electronic effects of exocyclic substituents could strongly influence π-delocalization in the fulvene ring. In compounds like pentafulvalene **5**, the π-system was localized, in compounds like nonatriafulvalene **10**, it was fully delocalized. In fact, aromaticity is cyclic π-delocalization, and, as *Fig. 12* showed, the π-system of a cyclic compound could be placed in the whole range between *non aromatic* (localized) and *aromatic* (fully delocalized). All the other 'terms of aromaticity' like '*quasi*-aromaticity', '*pseudo*-aromaticity', *etc.* are useless.[24]

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[24] The only term which has some (theoretical) legitimacy is *anti-aromaticity* [71]: A compound is said to be anti-aromatic if its *π-energy is raised by π-delocalization* (which is the case for cyclobutadienes). However, what happens in reality is that *the π-system stays localized*!

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