# 177. $^3J$(H,H) Coupling Constants as a Simple Criterion for π Delocalization of Pentafulvenes and Pentafulvalenes[1])

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A simple criterion for estimating the extent of π delocalization in the five-membered ring of pentafulvenes and pentafulvalenes is described. It is based on the fact that changes of bond lengths (induced by exocyclic substituents $R^1$–$R^2$ of **1**) are reflected by systematic changes of $^3J$(H,H) values, so that linear correlations of $\sigma_p^+$ *vs.* $^3J$(H,H) are obtained. Plots of that type (*Fig. 1*) are very useful for determining the extent of π delocalization of various pentafulvalenes **2**–**5** (*Fig. 3*) which show a very similar behavior to pentafulvenes. In principle, these plots could additionally be used for estimating substituent constants $\sigma_p^+$ or for approximating the extent of π overlap between exocyclic substituents and the π system of pentafulvenes. Charge-density effects of pentafulvenes and pentafulvalenes are observed by substituent-induced shifts of the ring C-atoms (*Fig. 4*).

**1. Introduction.** – Soon after the discovery of the first pentafulvenes by *Thiele* in 1900 [2], these molecules started to intrigue chemists. Although pentafulvenes are isomers of benzene, they show a surprisingly high reactivity towards a variety of reagents; furthermore, they are colored and have a dipole moment. As soon as the importance of *Hückel's* MO treatment [3] for conjugated π systems was recognized, numerous theoretical investigations concerning fulvenes were published. Early calculations seemed to indicate that in pentafulvenes bond lengths were less strongly alternating than in open-chain olefinic molecules, while a simple MO treatment predicted a dipole moment of 4.7 D for the parent compound [4], giving some importance to dipolar structures in the ground state. This result was easily accepted by experimental chemists, since reactivity of many fulvenes was compatible with an intermediate position between open-chain olefinic and delocalized aromatic molecules [5]. However, with increasing refinement of MO methods, theoretical predictions for parent fulvenes more and more supported molecules with strongly alternating bond lengths and a small dipole moment. So, for the parent pentafulvene the calculated dipole moment dropped from 4.7 [4] to 0.45 D [6], while MW investigations gave an experimental value of 0.424 D [7][2])!

Today all the spectroscopic data are in agreement with a basically olefinic character of parent pentafulvene which shows strongly alternating bond lengths, and is best represented by the canonical structure **1A**. On the other hand, exocyclic substituents $R^1$ and $R^2$ with electron-donating capacity might considerably enhance the importance of dipolar canonical structure **1B**, thus increasing π-bond delocalization as well as negative π-charge density in the ring. So the investigation of substituent effects on π delocalization of pentafulvenes is very attractive. Fortunately, contrary to heptafulvenes [1] and nonaful-

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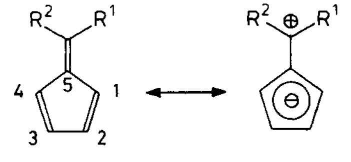
[1]) Fulvenes, Fulvalenes, Part 62; Part 61: [1].

[2]) For an illustrative discussion of older theoretical predictions see [8], pp. 168–184.



**1A** **1B**

**1a** $R^1 = R^2 = H$
**b** $R^1{-}R^2 = (CH_2)_4$
**c** $R^1{-}R^2 = S{-}CH_2{-}CH_2{-}S$
**d** $R^1{-}R^2 = O{-}CH_2{-}CH_2{-}O$
**e** $R^1 = EtO$; $R^2 = Me_2N$
**f** $R^1{-}R^2 = N(Me){-}CH_2{-}CH_2{-}N(Me)$

venes [9], the planar π system of pentafulvene is a well suited probe for such a task. One only has to look for good experimental criteria indicating changes in π delocalization[3]).

The results of extensive π delocalization in benzene are equal C–C bond lenghts of 1.398 Å, in contrast to cyclohexene where the C=C bond is 1.337 Å long, while adjacent C–C bonds are 1.543 Å long. So, *bond-length alternation* is a good qualitative criterion for deciding, whether a cyclic conjugated molecule is olefinic or aromatic[4]), provided that the data have been made available, *e.g.* from X-ray analysis or MW spectroscopy. While only a few structures of pentafulvenes have been determined so far by these methods (mainly due to thermal instability of the compounds), information about bond-length alternation may be provided by NMR spectroscopy as well: the size of *vicinal H,H coupling constants*, $^3J$(H,H), is strongly dependent on bond-lenghts, but unfortunately influenced by other factors as well [12], so that carefully selected molecules have to be compared (see later).

Highly delocalized cyclic molecules are characterized by an easy polarizability of the cloud of π electrons. In fact, *diamagnetic susceptibility* [13] may be taken as an indicator for aromaticity. The most famous effect induced by delocalized cyclic π systems is the *ring-current effect*, inducing a low-field shift for protons placed in the plane and outside of the ring. Unfortunately, $^1$H chemical shifts are not suited for the investigation of aromaticity of pentafulvenes, because, according to formula **1B**, an increased cyclic π delocalization is associated with an increased negative charge in the ring, thus inducing an opposite high-field shift.

Obviously $^3J$(H,H) values represent an accessible parameter[5]) which can be measured in dilute solutions of unstable compounds at low temperature. The main goal of this work is to show that $^3J$(H,H) values may be used for deriving the extent of π-bond delocalization (or aromaticity) in pentafulvenes and pentafulvalenes.

**2. Substituent Effects on $^3J$(H,H) Values of Pentafulvenes 1** (*Table*)[6]). – Vicinal H,H-coupling constants are strongly influenced by four parameters, namely *a*) the dihedral angle $\phi$, b) the H–C–C bond angle $\theta$, *c*) the electronegativity of substituents as

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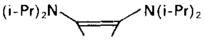
[3]) For a discussion concerning π-bond delocalization of fulvenes, see [10].

[4]) There are pitfalls, however, especially if X-ray simulates a totally delocalized structure, while in fact two of more partially delocalized structures are rapidly interconverting [11].

[5]) This is especially true for first-order NMR spectra of unsymmetrically substituted pentafulvenes. Symmetrical pentafulvenes and pentafulvalenes generate *AA'XX'*-type spectra of the ring protons which have to be carefully analyzed under high-resolution conditions.

[6]) These results have been presented in detail in [14]. They are summarized here, because they are indispensable as the basis of the envisaged aromaticity criterion. Generally, new is the idea of extrapolating *Hammett* plots of the type of *Fig. 1*, applying these plots to pentafulvalenes with unknown $\sigma^+$ and using them for deriving the extent of π delocalization. Plots of $^3J$(H,H) *vs.* *r*(C–C) are well known for other π-systems. For examples see [12] and quotations therein.

Table. *$^3J(H,H)$ Values and $^{13}C$ Chemical Shifts of Selected Pentafulvenes and Pentafulvalenes*

| Compound | $R^2$–$R^1$ | Y | $J(1,2)$ | $J(2,3)$ | $J(3,4)$ | C(1)/C(4) | C(2)/C(3) | C(5) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| **1b** | $CH_2$–$CH_2$–$CH_2$–$CH_2$ | H | 5.19a) | 2.03 | 5.19 | 121.1b) | 129.3 | 138.0 | [14] |
| **1c** | S–$CH_2$–$CH_2$–S | H | 4.95a) | 2.16 | 4.95 | 119.8b) | 128.5 | 132.3 | [14] |
| **1d** | O–$CH_2$–$CH_2$–O | H | 4.75a) | 2.31 | 4.75 | 118.0b) | 123.5 | 98.3 | [14] |
| **1e** | EtO $Me_2N$ | H | 4.53a) | 2.53 | 4.53 | 116.6b) | 117.6 | 103.4 | [14] |
| **1f** | $N(CH_3)$–$CH_2$–$CH_2$–$N(CH_3)$ | H | 4.21a) | 2.81 | 4.21 | 113.4b) | 114.0 | 98.6 | [14] |
| **3** | $(CH=CH)_2$ | H | 5.41c) | 1.99 | 5.41 | 122.0b) | 136.0 | 147.9 | [19] |
| **5** | $(CH=CH)_4$ | H | 5.32a) | 2.12 | 5.32 | 121.1a) | 132.1 | 143.0 | [20] |
| **4** | $(CH=CH)_3$ | H | 5.2d) | 2.2 | 5.2 | 118.6b) | 129.9 | 138.6 | [21] |
| **2b** |  | H | 4.7b) | 2.7 | 4.7 | 116.7b) | 121.1 | ? | [22] |
| **2c** |  | H | 4.0b)e) | 2.8e) | 4.0c) | 113.7b) | 112.7 | 98.2 | [22] |
| **2d** |  | CO–H | – | 3.25b) | 4.11 | | | | [23] |
| **2e** |  | $CO_2Et$ | – | 3.4b) | 3.8 | | | | [22] |
| **6** | (Dicalicene) | | – | 3.66 | 3.66 | | | | [24] |

a) $(D_6)$acetone. b) $CDCl_3$. c) $CD_2Cl_2$. d) $C_6D_6$. e) Coupling constants seem to be unreliable11).

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 $J(1,2)$, $J(2,3)$, and $J(3,4)$ should mainly reflect the electronic influence of substituents on bond lengths of the fulvene ring. Despite the fact that only a few X-ray structures of pentafulvenes have been determined so far, these results show that, compared with 6,6-dimethyl-pentafulvene [15], the effect of electron-releasing substituents at C(6) of **1** is an increase of the length of formal C=C bonds as well as a decrease of the length of formal single bonds in 6,6-bis(dimethylamino)pentafulvene [16]. Since there exists a linear relationship between bond lengths and $^3J$(H,H) values (of benzenoid compounds) on one side [12] as well as between bond lengths and MO bond orders on the other side [17], linear correlations between $^3J$(H,H) values and bond orders might be expected, as well. Due to the fact that X-ray results are missing in many cases, *Hammett* substituent constants $\sigma_p^+$ [18] are usually used as a measure of electronic substituent effects on bond lengths and bond orders.

A few years ago, we investigated the influence of exocyclic substituents on NMR parameters of pentafulvenes and showed that $^3J$(H,H) values are systematically influenced by substituents $R^1$ and $R^2$ [14]: whith increasing electron-donating capacity of the substituents, coupling constants $J(1,2)$ and $J(3,4)$ are decreasing, while $J(2,3)$ is increasing. Furthermore, linear correlations between $^3J$ values and *Hammett* substituent constants $\sigma^+$ are observed, which give good fits for exocyclically bridged pentafulvenes7) and poorer fits with more scattering for pentafulvenes with large substituents $R^1$ and $R^2$.

A very reasonable interpretation of the results of *Fig. 1* is that substituent effects influencing bond lengths (and bond orders) may be observed in terms of relative changes

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7) The *Hammett* plot of *Fig. 1* gives correlation coefficients of 0.992 for $J(1,2) = J(3,4)$ and of 0.998 for $J(2,3)$ [14].

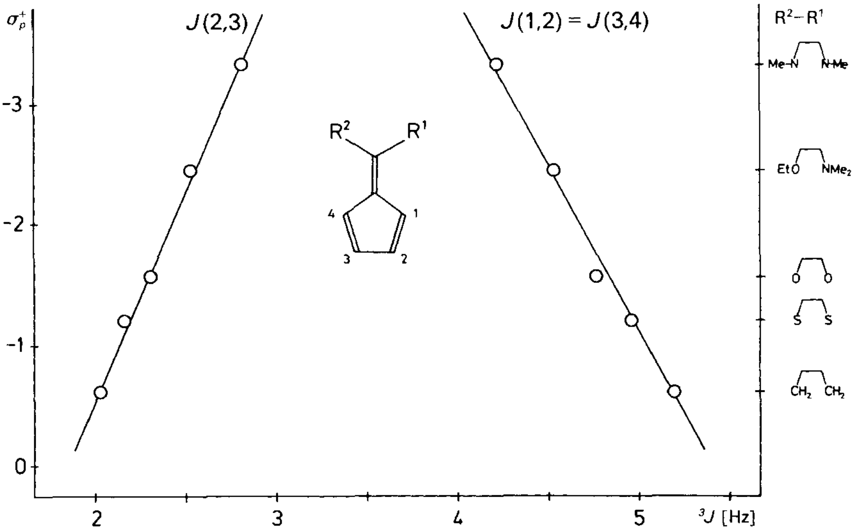


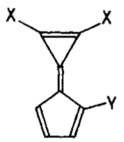
Fig. 1. *Plot of* $\sigma_p^+$ vs. *$^3$J(H,H) of 6,6-disubstituted pentafulvenes* **1b–f**

of $^3J$(H,H) provided that other effects are small, indicating that, in theses systems, the extent of $\pi$ delocalization is qualitatively accessible from $^3J$(H,H) values.

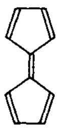
Obviously $^3J$(H,H) values of pentafulvenes are approaching with increasing $\pi$ delocalization according to *Fig. 1*. If this trend continues, then identical or at least very similar coupling constants would be expected for pentafulvenes with a complete $\pi$ delocalization in the five-membered ring. In fact, an extrapolation of *Fig. 1* gives a value of 3.43 Hz for identical coupling constants. $J(1,2) = J(2,3) = J(3,4)$. One only would like to have more data points, especially in the polar range beyond **1f**. A complete plot of that type could be very attractive for deriving the extent of $\pi$ delocalization of pentafulvenes from coupling constants.

**3. $\pi$ Delocalization of Pentafulvalenes.** – A first serious test for $\sigma^+$ *vs.* $^3J$ correlations of this type (*Fig. 1*) could be provided by systems where only small changes in charge-density and $\pi$ delocalization may be expected. This situation is typical for parent pentafulvenes **3** [25], **4** [26], and **5** [20] whose NMR-spectra have been analyzed [19–21].

Pentafulvenes are a special class of pentafulvenes in which $R^1$–$R^2$ consist of a bridge of conjugated C=C bonds which may enhance or decrease $\pi$ delocalization in the fulvene ring. According to the dipole moment of 2.2 D of heptapentafulvalene (**4**; compared with $\mu = 0.424$ D of **1a** [7]) the cycloheptatriene ring of **4** is slightly increasing the dipolar



**2**



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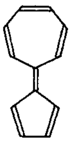

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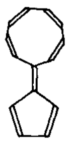
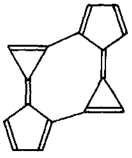


**5**



**6**

**2a** X = Y = H **2b** X = S–CMe$_3$, Y = H **2c** X = (CHMe$_2$)$_2$N, Y = H
**2d** X = Pr, Y = COH **2e** X = (CHMe$_2$)$_2$N, Y = COOEt

character as well as $\pi$ delocalization in the pentafulvene unit of **4**. On the other hand, the $\pi$ system of pentafulvalene (**3**) is expected to be somewhat more localized than that of pentafulvene, because the connected new diene unit should act as a weak electron-withdrawing substituent. Finally, nonapentafulvalene (**5**) should occupy an intermediate position between **3** and **4**. It is interesting to see, whether $^3J$ will reflect such comparably small electronic substituent effects.

One serious problem concerning plotting of pairs of coupling constants $J(1,2)/J(3,4)$ of pentafulvalenes against $\sigma_p^+$ seems to stem from the fact that *Hammett* substituent constants of the diene, triene, and tetraene bridges of **3**, **4**, and **5**, respectively, are not known. Therefore, a modified procedure has to be adopted for the generation of pentafulvalene plots which is illustrated in *Fig. 2* and makes use of the pentafulvene plot of *Fig. 1* (black slopes): for each compound, the set of coupling constants $J(1,2)/J(2,3)$ is entered, and the intersections with the two slopes of the pentafulvene plot are marked. Since there is only one correct (but unknown) $\sigma_p^+$ value for each bridge, the pair of intersections of each compound has to be averaged to the best horizontal line giving the black circles in *Fig. 2*8).

The results (*Fig. 2*) hint to the conclusion9) that pentafulvalenes **3**–**5** show the same substituent-induced slopes of vicinal H,H-coupling constants (dotted lines) as pentafulvenes (**1**); but there seems to be a small but systematic difference between both slopes of at *ca.* 0.1 Hz. Obviously, the difference of $^3J$(H,H) values is most pronounced for pentafulvalene (**3**), and it slightly decrease from **3** to **5** and to **4**. This means that $\pi$ delocalization is very small for parent **3**, and that is slightly but steadily increases from **3** to nonapentafulvalene (**5**) and to heptapentafulvalene (**4**). This is exactly the expected trend (see above):

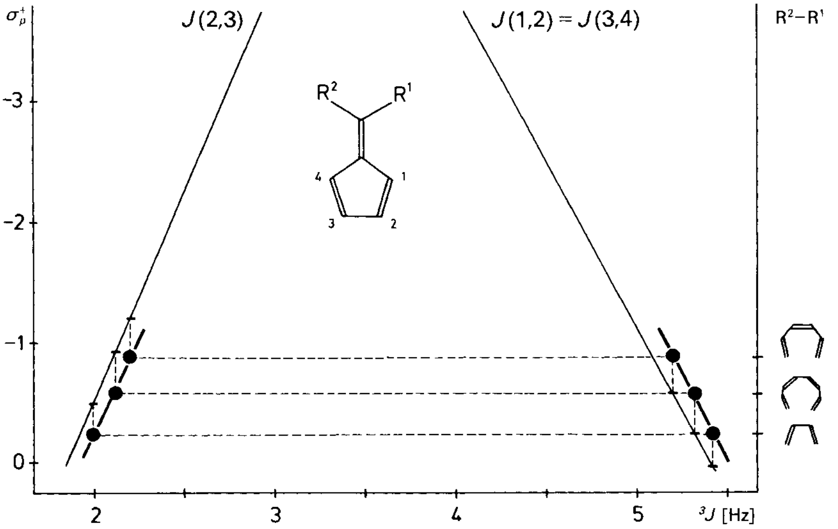


Fig. 2. *$^3J$(H,H) Values of pentafulvalenes **3**–**5**, compared with substituent-induced slopes of pentafulvenes*

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8) In principle, this method allows the determination of unknown substituent constants.

9) This conclusion is quite weak as long as only sets of $^3J$ values of pentafulvalenes **3**, **4**, and **5** are compared, because all three sets of coupling constants are close together; it is much stronger as soon as more delocalized calicenes **2** are considered as well (see later).

while **3** is definitely more localized than 6,6-dimethylpentafulvene, **4** is somewhat more delocalized.

For completing the series of pentafulvalenes, the still unknown pentatriafulvalene ( = calicene; **2a**) would be very interesting, because the electron-releasing power of the bridged C=C bond of **2** is assumed to be stronger than that of the triene unit of **4**[10]. Unfortunately, calicene **2a** is still unknown, and there are only a few known calicenes having at least three vicinal protons in the ring. In the same way as discussed above, the coupling constants of 5,6-di(*tert*-butylthio)calicene (**2b**) [22] as well as of 1-formyl-5,6-dipropylcalicene **2d** [23] are entered in the plot[11]. As *Fig. 3* shows, both sets of coupling constants are perfectly fitting with the pentafulvalene slope, showing the same slight deviation from the fulvene slope as pentafulvalenes **3**–**5**. This perfect fit allows to mark the intersection of the two slopes giving $J(1,2) = J(2,3) = 3.65$ Hz for a complete $\pi$ delocalization in the five-membered ring of pentafulvalenes. This value perfectly matches the experimental result of $J(1,2) = J(2,3) = 3.66$ Hz of dicalicene (**6**) which seems to be fully delocalized according to X-ray data [24].

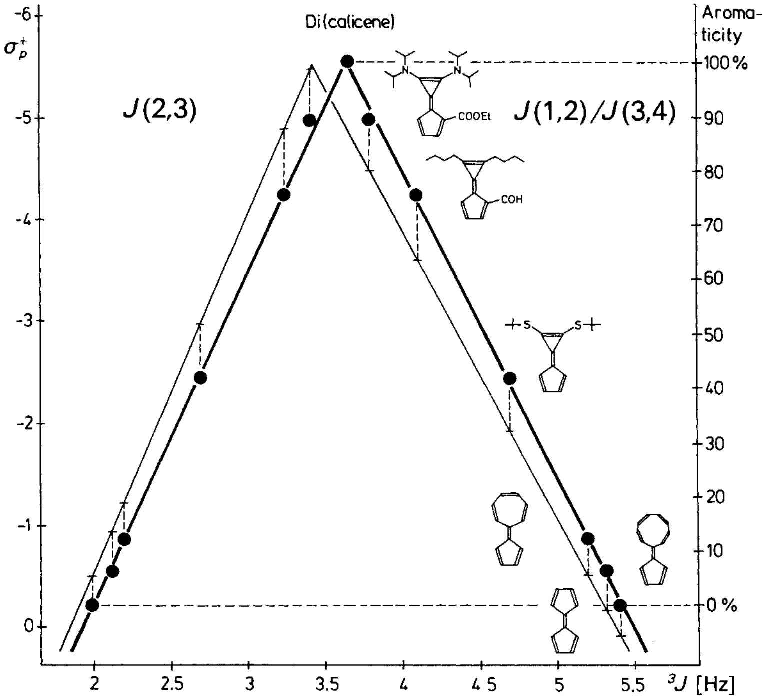

Fig. 3. *Substituent-induced slopes* ($\sigma_p^+$ *vs.* $^3J$(H,H)) *of pentafulvenes* **1** (thin lines) *and of pentafulvalenes* **2**–**5** *and dicalicene* (**6**; bold lines)[12]

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[10] This is seen by analogy: the dipole moment of triafulvene ($\mu$ = 1.90 D [27]) is considerably larger than that of heptafulvene ($\mu$ = 0.477 D [28]), while both rings are positively polarized.

[11] Contrary to calicenes **2b**, **2d**, and **2e**, the coupling constants of 5,6-bis(diisopropylamino)calicene **2c** give a rather poor fit with the slopes of *Fig. 3*. Due to the fact that only a badly resolved *AA'BB'* system (60-MHz spectrum) has been approximately analyzed [22], this set of coupling constants is considered to be quite unreliable.

[12] $\sigma_p^+$ Values are those of the substituents of pentafulvenes.

Diagrams like *Fig. 3* might be very useful for estimating the extent of $\pi$ delocalization (or aromaticity) of pentafulvalenes (thin lines) and pentafulvalenes (bold lines) from $^3J$(H,H) values: obviously the crossing of the lines of each slope marks equal coupling constants $J(1,2) = J(3,4)$; it corresponds to a completely delocalized $\pi$ system or to a compound which is a 100% aromatic. There is more discussion about which set of $^3J$ coupling constants would correspond to a localized pentafulvene with an aromaticity of 0%. Clearly, pentafulvalene (**3**) has the highest localized $\pi$ system of all the compounds given in the *Table*, and the contribution of the dipolar form (see **1B**) to the ground state is reduced to 0[13]. Because of that we propose to take the experimental $^3J$ values of **3** for marking a 0% aromaticity on the abscissa of *Fig. 3*[14].

**4. Discussion.** – In this work, we propose a simple and straightforward aromaticity criterion for pentafulvenes and pentafulvalenes which is based on the fact that linear correlations are observed between *Hammett* substituent constants $\sigma_p^+$ and $^3J$(H,H) values of exocyclically bridged pentafulvenes **1b–f** [14]. This plot (*Fig. 1* and thin lines of *Fig. 3*) is easily available according to the data of the *Table* and well-known $\sigma_p^+$ values of substituents[15]. It serves as basic plot for constructing the pentafulvalenes slopes of *Fig. 3* (bold lines): $^3J$(H,H) values of pentafulvalenes are entered into *Fig. 3*, and the intersections with the pentafulvene plot are averaged to the best horizontal line.

6,6-Disubstituted *pentafulvenes* are directly entered into the plot of *Fig. 3* (thin lines) according to their coupling constants and $\sigma_p^+$ values. For exocyclically bridged pentafulvenes (where steric effects are minimized, and electronic effects are fully operative), a good fit with the pentafulvene slopes is expected. There may be a considerable scattering for 6,6-disubstituted pentafulvenes with sterically different environment, or as soon as the lone-pairs of exocyclic substituents do not have a good overlap with the $\pi$ system of the fulvene. The plot allows the determination of the extent of $\pi$ delocalization (right-$y$ axis) from $^3J$ values. This is possible even if the $\sigma_p^+$ constants are not known (or wrong due to an insufficient $\pi$ overlap of substituents): in this case, $^3J$ values are entered into the pentafulvene plot and averaged to the best horizontal line (see procedure for pentafulvalenes).

The plot for *pentafulvalenes* (bold lines) convincingly shows that even small electronic influences of conjugated bridges are visible (see parent pentafulvalenes **3–5**). It allows to estimate the extent of $\pi$ delocalization of new pentafulvalenes, and, for the compounds entered into *Fig. 3*, shows a surprisingly small deviation of the pairs of $^3J$ values from the pentafulvalene slope. As for pentafulvenes more scattering is expected as soon as steric

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[13] Note that, according to canonical structures $\mathbf{1A} \leftrightarrow \mathbf{1B}$, an increasing dipolar character of pentafulvenes is associated with an increasing $\pi$ delocalization in the ring!

[14] Another possibility is to take a $\sigma^+ = 0$ (or the corresponding extrapolated coupling constants) as a basis for a pentafulvene (pentafulvalene) with a localized $\pi$ system. Anyhow, the difference between both zero points is very small according to *Fig. 3* (and neglectable according to the $\sigma^+$ *vs.* $\delta(^{13}C)$ plot of *Fig. 4*). This is illustrated by the following reasoning: a very slight change of coupling constants of pentafulvalene **3** from 1.99 to 1.93 ($J(2,3)$) and from 5.41 to 5.48 Hz ($J(1,2)$) would, after entering into *Fig. 3*, give a zero point on the abscissa which would be identical to $\sigma_p^+ = 0$!

[15] The following literature data [18] of *Hammett* substituent constants $\sigma_p^+$ have been used for $R^1-R^2$: Me: –0.31; MeS: –0.60; MeO: –0.78; $Me_2N$: –1.67. Substituent effects are assumed to be approximately additive, so that $\sigma_p^+ = -1.20$ is taken for **1c**, *etc.* This seems to be justified by the fact that a $\sigma_p{}^+ =$ *vs.* $J(2,3)$ plot of all the 6-monosubstituted, 6,6-disubstituted, and exocyclically bridged 6,6-disubstituted pentafulvenes gives a satisfactory correlation coefficient of 0.929, despite of the observed scattering due to steric effects [29].

effects of substituents would be operative. On the other hand, a reduced $\pi$ overlap of substituents with the ring system would not necessarily induce a deviation of the $^3J$ pairs from the pentafulvalene slope: it would clearly result in a decrease of $J(2,3)$, but simultaneously in an increase of $J(1,2)$, so that the pair of coupling constants would occupy a somewhat lower position of the slope than expected, being consistent with the reduced $\pi$ delocalization. This special way of plotting $^3J$ values of pentafulvalenes according to the real electronic substituent effect (influencing $\Delta J$) is certainly one major reason for the considerably reduced scattering of the data points of the pentafulvalene slopes[16]) compared with the pentafulvene slopes (see *Figs. 3* and *1*).

It should be pointed out that, strictly speaking, plots of *Fig. 3* are expected to give good correlations only for pentafulvenes and pentafulvalenes with four adjacent protons in the five-membered ring: not only have pentafulvene plots of *Fig. 1* been obtained for 6,6-disubstituted pentafulvenes without substituents in the ring, but large substituents at C(1) with extreme steric and/or electronic effects could influence the size of $^3J$ coupling constants. It seems that CO groups at C(1) are acceptable, since the data sets of calicenes **2d** and **2e** are quite nicely fitting into the plot, and the same is obviously true for bicalicene **6** (*cf. Fig. 3*). On the other hand, the $NO_2$ group is quite dangerous because of strong stereoelectronic effects, and in fact the $^3J$ values of 7,8-bis(diisopropylamino)-1-nitrocalicene ($J(2,3) = 3.3$; $J(3,4) = 4.4$ [22]) deviate quite strongly from the plot of *Fig. 4*. In any case, coupling constants should be reliable in the range of ±0.03 Hz. This is certainly not reconfirmed for calicenes **2c**[11]) and **2e** [22] where *AA'XX'* and *AMX* systems should be re-analyzed[17]).

Finally, the question has to be discussed, whether the difference between the slopes of pentafulvenes and pentafulvalenes (*Fig. 3*) is significant or within the range of normal scattering. According to *Fig. 3*, $^3J$ values of pentafulvenes are slightly smaller by *ca.* 0.15 Hz compared with pentafulvalenes of the same $\sigma_p^+$. Since correlations of $\sigma_p^+$ *vs.* $^3J$ are good for pentafulvenes (*Fig. 1*)[7]) and excellent for pentafulvalenes (*Fig. 3*), the difference seems to be systematic. A reasonable explanation is based on the fact that for pentafulvenes some residual electronegativity effect of substituents $R^1$–$R^2$ is still operative. In this case, both $J(2,3)$ and $J(1,2) = J(3,4)$ are expected to be slightly smaller than for pentafulvalenes, and that exactly matches the observed trends.

**5. Substituent Effects on $^{13}$C Chemical Shifts of Pentafulvalenes.** – Recently, we have shown that $^{13}$C-chemical shifts of the ring-C-atoms of pentafulvenes **1** are strongly influenced by exocyclic substituents $R^1$–$R^2$ [14]: with increasing electron-donating capacity of the substituents, a systematic high-field shift of C(1)–C(5) is observed which strongly decreases in the series C(5) > C(2)/C(3) > C(1)/C(4). Additionally, linear plots of $\sigma_p^+$ *vs.* $\delta(^{13}C)$ are obtained for C(1)/C(4) and C(2)/C(3) of exocyclically bridged pentafulvenes which are shown in *Fig. 4* (bold lines). Although the substituent-induced trend of C(5) is obvious according to the data of the *Table*, there is much more scattering,

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[16]) On the other hand, a significant deviation of the $^3J$ pair from the pentafulvalene slopes could be indicative for an erroneous analysis of the *AA'XX'* system of the protons of the five-membered ring (see **2**, Y=H). This could be the case for calicene **2c** where both coupling constants, after entering into *Fig. 3*, seem to be too small[11]) by 0.16 ($J(2,3)$) and 0.38 Hz ($J(1,2)$).

[17]) On the other hand $^3J$ values of calicene **2b** (see the *Table* [22]) are quite reliable, since our re-investigation gave $J(1,2) = J(3,4) = 4.57$ and $J(2,3) = 2.61$ Hz (400 MHz, $CDCl_3$) [30].

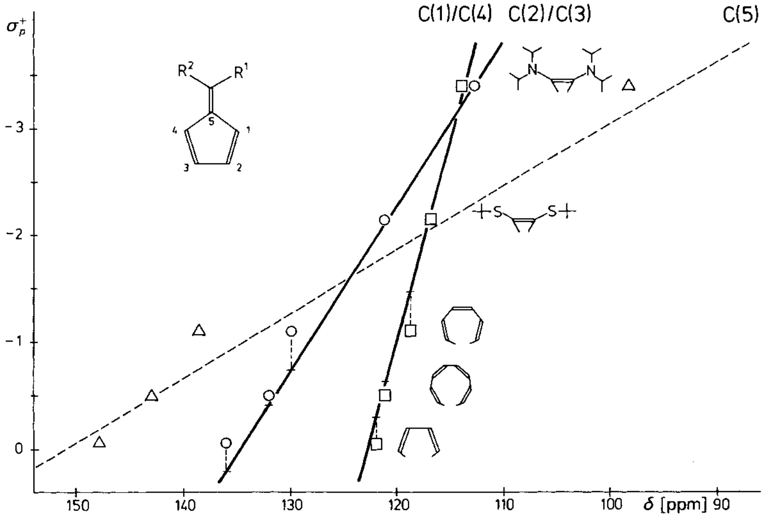

Fig. 4. *Substituent-induced slopes* ($\sigma_p^+$ *vs.* $\delta$($^{13}$C)) *of C(5)* (dotted lines) *C(2)/C(3) and C(1)/C(4)* (bold lines) *of pentafulvenes* **1b–f** *containing the* $\delta$($^{13}$C) *values of pentafulvalenes* **3–5**, **2b**, *and* **2c** (C(5): △; C(2)/C(3): ○; C(1)/C(4): □)[18])

probably mainly due to steric effects. A tentative correlation of C(5) is given in *Fig. 4* (dotted lines) too[18]).

These substituent-induced high-field shifts of pentafulvenes have been convincingly explained as charge-density effects [14]. HMO Calculations show that substituent effects on charge density of pentafulvenes may be simulated by introducing an $\alpha$-disturbance at C(6). Increasing the heteroatom parameter of C(6) simulates an electron-accepting group and influences charge-density at the ring-C-atoms. This influence strongly decreases in the series C(5) > C(2)/C(3) > C(1)/C(4).

If pentafulvalenes are behaving similarly to pentafulvenes (and there is good evidence from $^3J$ values, see above), then the $^{13}$C-NMR data should reflect the same trends. However, once again there is the problem of entering the shifts of compounds of unknown substituent constant $\sigma_p^+$ into the plot of *Fig. 4*. It is resolved similarly to the plots of *Figs. 2* and *3*[19])[20]) so that the sets of data points of each pentafulvalene are available (*Fig. 4*)[8]).

According to *Fig. 4*, pentafulvalenes show the same substituent-induced high-field shifts as pentafulvenes which strongly decrease in the row C(5) > C(2)/C(3) > C(1)/C(4), and which are best explained by charge-density effects (see later). For unpolar pentaful-

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[18]) In this correlation, the very surprising high-field absorption of C(5) of **1d** has not been included. The correlation of C(5) is quite unsafe due to the scattering of data.

[19]) The following procedure for entering $^{13}$C-chemical shifts of pentafulvalenes of unknown $\sigma_p^+$ into the plot of *Fig. 4* has been adopted[8]): for each compound, the set of $^{13}$C-chemical shifts $\delta$ of C(1)/C(4) and C(2)/C(3) is entered, and the intersections with the two slopes of the pentafulvene plot (bold lines) are marked. Since there is only one correct (but unknown) $\sigma_p^+$ value for each exocyclic bridge, the pair of intersections of each compound has to be averaged to the best horizontal line giving the points ○ as well as □. $\Delta$ of C(5) is entered at the same horizontal line[20]).

[20]) Due to the fact that the slope of C(5) is very unsafe because of 'steric scattering', only the correlations of C(1)/C(4) and C(2)/C(3) of pentafulvenes **1** have been used as reference slopes.

valenes, C(5) is at highest frequency followed by C(2)/C(3) and C(1)/C(4); however, due to the different slopes of correlations of *Fig. 4*, a completely reversed sequence of C-atoms has to be expected for polar pentafulvalenes so that assignments have to be made with care. If $\sigma_p^+$ *vs.* $\delta(^{13}C)$ correlations would be drawn only by means of the pentafulvalene data, then the plot of C(1)/C(4) would be nearly identical with the pentafulvene plot (bold line) while the slope of C(2)/C(3) would be somewhat more pronounced for pentafulvalenes. Similarly to pentafulvenes, the correlation coefficient of the pentafulvalene plots decrease in the series C(1)/C(4) > C(2)/C(3) > C(5).

As *Fig. 4* convincingly shows, pentafulvalene (**3**; whose dipole moment is zero) is placed at the unpolar end of the fulvalene series and, similarly to the $^3J$ plots of *Figs. 2* and *3*, the substituent constant $\sigma_p^+$ of the diene bridge[8]) is close to zero. As in *Figs. 2* and *3* $^3J$ values are moderately approaching, negative charge density of five-ring-C-atoms is moderately increasing from pentafulvalene (**3**) to nonapentafulvalene (**5**) and heptapentafulvalene (**4**). Finally, the five-membered ring of calicene (**2c**) is already strongly polarized according to *Fig. 4*: the chemical shifts of **2c** are corresponding to a $\sigma_p^+$ value of 3.4 which is very close to that of pentafulvene **1f**, which by itself has an aromaticity of *ca.* 60% according to *Fig. 3*.

Plots of *Figs. 3* and *4* could generally be useful for estimating $\sigma^+$ constants[8]). This method is somewhat hampered so far by the scattering of NMR data, it could become very interesting as soon as more data are known, thus increasing the reliability of the plots. The method is very attractive even for pentafulvenes **1** with substituents of known $\sigma^+$ value which do not give a complete $\pi$ overlap due to steric reasons. In this case, the electronic substituent effect would be smaller than expected according to the $\sigma^+$ value of the literature [18]. Entering the experimental $^3J$(H,H) values into the plot of *Fig. 3* or the $^{13}C$ chemical shifts into the plot of *Fig. 4* could, in principle, give realistic $\sigma_p^+$ values corresponding to the real extent of $\pi$ overlap of the substituent. The actual 'state of art' is seen from the approximate substituent constants derived from the olefinic bridge of pentafulvalenes out of *Figs. 3* and *4*: horizontal extrapolation from $^3J$ plots of *Fig. 3* (or $\delta(^{13}C)$ plots of *Fig. 4*) gives a $\sigma^+$ of −0.20 (−0.06) for **1**; −0.55 (−0.62) for **5**; −0.86 (−1.11) for **4**; −2.44 (−2.14) for **2b** and −3.34 (−3.40) for **2c**. This result convincingly shows that the plots of *Figs. 3* and *4* are corresponding.

According to the $^1H$- (*Fig. 3*) and $^{13}C$-NMR results (*Fig. 4*), pentafulvalenes are spectroscopically behaving very similarly to pentafulvenes: they show the same substituent-induced trend of $^3J$(H,H) values, and from plots of *Fig. 3* the extent of $\pi$ delocalization or aromaticity is easily available. Furthermore, charge-density effects are seen from changes of $^{13}C$-chemical shifts, and the substituent-induced relative sensitivity of C(5) > C(2)/C(3) > C(1)/C(4) is completely compatible with changes of $\pi$ charge density available from HMO calculations [31]. With increasing accuracy of plots of *Figs. 3* and *4* realistic substituent constants $\sigma^+$ might be available, thus reflecting the extent of $\pi$ overlap of exocyclic substituents. All these results demonstrate that the planar $\pi$ system of pentafulvenes and pentafulvalenes is a fantastic tool for the investigation of electronic substituent effects.

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## Experimental Part

*Syntheses.* Pentafulvenes and Pentafulvalenes have been prepared according to literature procedures: **1b**: [32]; **1c**: [33]; **1d** synthesis is similar to that of 6,6-dimethoxypentafulvene [34]; **1e**: [34]; **1f**: synthesis is similar to that of 6,6-bis(dimethylamino)pentafulvene [34]; **3**: [25]; **4**: [26]; **5**: [20].

*$^1$H-NMR Spectra.* The analysis of *AA'XX'*-type spectra of pentafulvenes and fulvalenes has been described in [19]. NMR Data have been taken out of the following papers: **1a**–**1f**: [14]; **2b**: [22]; **2c**: [22]; **2d**: [23]; **3**: [19]; **4**: [21]; **5**: [20]; **6**: [24].

## REFERENCES

[1] P. Bönzli, M. Neuenschwander, *Helv. Chim. Acta* **1991,** *74,* 255.

[2] J. Thiele, *Chem. Ber.* **1900,** *33,* 666; J. Thiele, H. Balhorn, *Liebigs. Ann. Chem.* **1906,** *348,* 1.

[3] E. Hückel, *Z. Phys.* **1931,** *70,* 204.

[4] A. Pullman, B. Pullman, P. Rumpf, *Bull. Soc. Chim. Fr.* **1948,** 757.

[5] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, K. H. Vöpel, *Angew. Chem.* **1963,** *75,* 35; *ibid. Int. Ed.* **1963,** *2,* 123.

[6] P. A. Straub, D. Meuche, E. Heilbronner, *Helv. Chim. Acta* **1966,** *49,* 517.

[7] P. A. Baron, R. D. Brown, F. E. Burden, J. J. Domaille, J. E. Kent, *J. Mol. Spectrosc.* **1972,** *43,* 401.

[8] P. Yates, in 'Advances in Alicyclic Chemistry', Ed. H. Hart, Academic Press, New York, Vol. 2, pp. 59–184.

[9] A. Otter, G. Sabbioni, M. Neuenschwander, H. P. Kellerhals, *Helv. Chim. Acta* **1986,** *69,* 12; J. Furrer, P. Bönzli, A. Frey, M. Neuenschwander, *ibid.* **1987,** *70,* 862: A. Otter, M. Neuenschwander, H. P. Kellerhals, *Magn. Reson. Chem.* **1986,** *24,* 353.

[10] M. Neuenschwander, 'Fulvenes', in 'The Chemistry of Double-bonded Functional Groups', Ed. S. Patai, John Wiley, London, 1989, p. 1131–1268.

[11] O. Ermer, *Angew. Chem.* **1987,** *99,* 791; *ibid. Int. Ed.* **1987,** *26,* 782.

[12] H. Günther, 'NMR-Spektroskopie', Thieme, Stuttgart, 1983; H. Günther, H. Schmickler, M.-E. Günther, D. Cremer, *Org. Magn. Reson.* **1977,** *9,* 420.

[13] J. A. Elvidge, L. M. Jackman, *J. Chem. Soc.* **1961,** 859.

[14] P. Bönzli, A. Otter, M. Neuenschwander, H. Huber, H. P. Kellerhals, *Helv. Chim. Acta* **1986,** *69,* 1052.

[15] H. L. Ammon, *Acta Crystallogr., Sect. B* **1974,** *30,* 1731.

[16] R. Böhme, H. Burzlaff, *Chem. Ber.* **1974,** *107,* 832.

[17] E. Heilbronner, H. Bock, 'Das HMO-Modell und seine Anwendungen', Verlag Chemie, Weinheim, 1968.

[18] L. P. Hammett, 'Physical Organic Chemistry', Mc Graw Hill, New York, 1940; H. C. Brown, Y. Okamoto, *J. Am. Chem. Soc.* **1958,** *80,* 4979; C. G. Swain, E. C. Lupton, *ibid.* **1968,** *90,* 4328.

[19] A. Escher, P. Bönzli, A. Otter, M. Neuenschwander, *Magn. Reson. Chem.* **1968,** *24,* 350.

[20] A. Escher, M. Neuenschwander, *Helv. Chim. Acta* **1987,** *70,* 49.

[21] R. Hollenstein, A. Mooser, M. Neuenschwander, W. von Philipsborn, *Angew. Chem.* **1974,** *86,* 595; *ibid. Int. Ed.* **1974,** *13,* 551.

[22] Z. Yoshida, *Pure Appl. Chem.* **1982,** *54,* 1059; S. Miki, Dissertation, Kyoto University, 1978, S. Araki, Dissertation, Kyoto University, 1978.

[23] A. S. Kende, *Trans. New York Akad. Sci.* **1966,** *28,* 981.

[24] S. Yoneda, M. Shibata, S. Kida, Z. Yoshida, K. Miki, N. Kasai, *Angew. Chem.* **1984,** *96,* 75; *ibid. Int. Ed.* **1984,** *23,* 63.

[25] A. Escher, W. Rutsch, M. Neuenschwander, *Helv. Chim. Acta* **1986,** *69,* 1644.

[26] W. K. Schenk, R. Kyburz, M. Neuenschwander, *Helv. Chim. Acta* **1975,** *58,* 1099.

[27] T. D. Norden, S. W. Staley, W. H. Taylor, M. D. Harmony, *J. Am. Chem. Soc.* **1986,** *108,* 7912.

[28] A. Bauder, C. Keller, M. Neuenschwander, *J. Mol Spectrosc.* **1976,** *63,* 281.

[29] P. Bönzli, Diploma Work, University of Bern, 1983.

[30] D. Guggisberg, Dissertation, University of Bern, 1989.

[31] H. Huber, personal communication (Institute of Physical Chemistry, University of Basel).

[32] E. P. Kohler, J. Kable, *J. Am. Chem. Soc.* **1935,** *57,* 917.

[33] K. Hartke, E. Schmid, M. Castillo, J. Bartulin, *Chem. Ber.* **1966,** *99,* 3268.

[34] K. Hafner, G. Schulz, K. Wagner, *Liebigs. Ann. Chem.* **1964,** *678,* 39.