

13. ^1H - and ^{13}C -NMR Investigation of Nonafulvenes¹⁾

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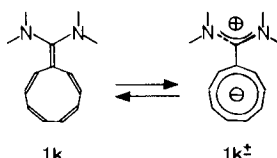
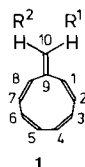
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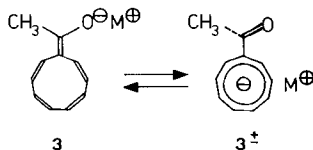
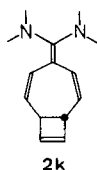
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^1H - and ^{13}C -NMR spectra of a series of nonafulvenes **1** have been investigated. Most nonafulvenes are olefinic molecules with alternating bond lengths, their nine-membered ring deviating strongly from planarity. The 10-monosubstituted nonafulvenes contain 2 sterically different ring segments with a nearly planar (*E*)-diene system consisting of C(7), C(8), C(9), C(10), and R. Substituents R are influencing C(9) > C(7) > C(5). In symmetrically substituted nonafulvenes a fast process equilibrating olefinic conformers is operating so that pairs of ring protons and ring C-atoms are equivalent and only average substituent effects are observed for C(9) > C(7,2). ^1H - and ^{13}C -NMR chemical shifts are not significantly influenced by changes of solvent or temperature. On the other hand, new ^{13}C - and ^1H -NMR experiments completing previous investigations by *Hafner* and *Tappe* confirm that NMR spectra of 10,10-bis(dialkylamino)nonafulvenes are strongly dependent on solvent polarity and temperature. At ambient temperature and in unpolar solvents, nonplanar conformers are predominant, their spectral data fitting into the series of other nonafulvenes. At low temperature and/or in polar solvents, dipolar conformers are favoured which are characterised by charge separation and a planarised (but not necessarily completely planar) nine-membered ring with negative excess charge. The spectroscopic behaviour of nonafulvenes is reasonably explained by a qualitative scheme (*Fig. 7*) which is based on a model proposed by *Boche* for nonafulvenolates.

Introduction. – Nonafulvene (**1a**) [2] as well as the electronically stabilised 10,10-bis-(dimethylamino)nonafulvene (**1k**) [3] have a surprisingly different spectroscopic behav-



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|-----------|---------------------------------------------------------------|-----------|---------------------------------------------------------------------------------------|
| 1a | $\text{R}^1 = \text{R}^2 = \text{H}$ | 1g | $\text{R}^1 = \text{R}^2 = \text{CH}_3\text{O}$ |
| 1b | $\text{R}^1 = \text{C}_6\text{H}_5, \text{R}^2 = \text{H}$ | 1h | $\text{R}^1, \text{R}^2 = \text{OCH}_2\text{CH}_2\text{O}$ |
| 1c | $\text{R}^1 = \text{CH}_3\text{O}, \text{R}^2 = \text{H}$ | 1i | $\text{R}^1 = \text{CH}_3\text{S}, \text{R}^2 = (\text{CH}_3)_2\text{N}$ |
| 1d | $\text{R}^1 = (\text{CH}_3)_2\text{N}, \text{R}^2 = \text{H}$ | 1j | $\text{R}^1 = (\text{C}_2\text{H}_5)_2\text{N}, \text{R}^2 = (\text{CH}_3)_2\text{N}$ |
| 1e | $\text{R}^1 = \text{R}^2 = \text{CH}_3\text{S}$ | 1k | $\text{R}^1 = \text{R}^2 = (\text{CH}_3)_2\text{N}$ |
| 1f | $\text{R}^1, \text{R}^2 = \text{SCH}_2\text{CH}_2\text{S}$ | | |



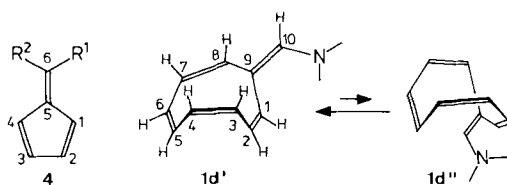
¹⁾ Fulvenes, Fulvalenes, Part 47; for Part 46, see [1].

our. While the UV and $^1\text{H-NMR}$ data of **1a** are compatible with a nonplanar olefinic molecule and are not significantly influenced by solvent or temperature effects [4], the spectroscopic properties of **1k** are strongly influenced by changes of solvents or temperature [3] [5] [6]. This remarkable behaviour of **1k** has been attributed to a fast equilibrium between 2 spectroscopically different species [5]. However, a first tentative explanation assuming an equilibrium between **1k** and its valence isomer **2k** [5] had to be abandoned in the light of new 220-MHz NMR experiments [6], where pairs of ring protons were assigned. *Tappe* [6] favoured an equilibrium between 2 conformers, 'the more planar conformer being favoured in polar solvents and/or at low temperature, the less planar conformer existing in unpolar solvents at higher temperatures'.

Solvent and temperature effects of such an extent are not known so far in other cross-conjugated systems such as pentafulvenes **4** or heptafulvenes. On the other hand, similar effects have been observed by *Boche et al.* [7] for acyl-cyclononatetraenides and have been attributed to an equilibrium between the nonafulvenolate **3** existing as contact ion-pair, and the solvent separated ion pair of the acyl-cyclononatetraenide **3[±]**, the latter being preferred in polar solvents at low temperature. Subsequently, *Boche* suggested a similar equilibrium between **1k** and **1k[±]** [7] [8].

In view of a more detailed NMR investigation of the surprisingly different behaviour of nonafulvenes **1a** and **1k**, a series of 10-substituted and 10,10-disubstituted nonafulvenes filling the gap between **1a** and **1k** have been prepared [8] [9]. However, because of the complexity of the $^1\text{H-NMR}$ spectra, only a few protons have been assigned [8], and detailed $^{13}\text{C-NMR}$ assignments were missing so far. Very recently, the analysis of the $^1\text{H-NMR}$ spectrum of 10-(dimethylamino)nonafulvene **1d** [8] has been completed [1]. The results show that **1d** is not planar and contains 2 sterically very different ring segments with a nearly planar (*E*)-dienamine moiety N, C(10), C(9), C(8), C(7). In the conformational equilibrium **1d' ⇌ 1d''**, **1d'** is favoured because of steric reasons.

Here, we wish to report the results of a $^1\text{H-}$ and $^{13}\text{C-NMR}$ analysis of nonafulvenes **1b–j** [10]. Substituent effects on $^1\text{H-}$ and $^{13}\text{C-NMR}$ chemical shifts and H,H-coupling constants will be discussed, and some new results concerning 10,10-bis(dimethylamino)nonafulvene (**1k**) will be presented.



Results and Discussion. – The results of the analysis of $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra of nonafulvenes **1b–i** are listed in *Tables 1–5* and compared with those of nonafulvenes **1a** [4] and **1k** [6]. Substituent effects on chemical shifts and coupling constants are illustrated in *Fig. 1–3*, where δ and J values are plotted against *Hammitt* substituent constants σ^+ [11]. Diagrams of that type show nearly linear correlations of $^{13}\text{C-NMR}$ shifts and $^3J(\text{H,H})$ coupling constants (but not of $^1\text{H-NMR}$ shifts) for sterically similar pentafulvenes **4** [12] [13].

Table 1. $^1\text{H-NMR}$ Chemical Shifts (± 0.01 ppm, relative to TMS) of Nonafulvenes **1a–k**

Compound	H–C(1) / H–C(8)	H–C(2) / H–C(7)	H–C(3) / H–C(6)	H–C(4) / H–C(5)	H–C(10)
1a ^{a)}	6.12	5.63	5.99	5.82	5.11
1b ^{b)}	6.35 6.14	6.06 ^{c)} 5.68	6.26 6.06 ^{c)}	6.06 ^{c)} 5.82	6.55
1c ^{d)}	6.27 5.76 ^{e)}	5.86 5.43	6.18 6.03	6.00 5.76 ^{e)}	6.27
1d ^{e)}	6.34 5.70	5.87 5.07	6.11 5.94	6.05 5.55	5.98
1e ^{b)}	6.65	5.80	6.09	5.89	–
1f ^{d)}	6.12	5.64	6.05	5.85	–
1g ^{f)}	6.11	5.55	6.06	5.82	–
1h ^{f)}	6.07	5.42	6.03	5.78	–
1i ^{d)}	6.23	5.56	6.12	5.84	–
1k ^{g)}	5.72	5.41	6.28	5.92	–

^{a)} (D_6)Acetone, -30° . ^{b)} CDCl_3 , -40° . ^{c)} Overlap with other signals. ^{d)} CDCl_3 , -30° . ^{e)} CDCl_3 , -10° . ^{f)} CD_2Cl_2 , -40° . ^{g)} CDCl_3 , 0° , the equilibrium $\mathbf{1k} \rightleftharpoons \mathbf{1k}^{\pm}$ is mainly (but not completely) on the side of $\mathbf{1k}$.

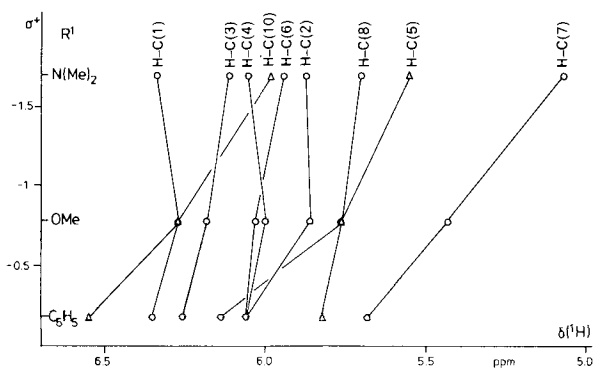


Fig. 1. Substituent effects on $^1\text{H-NMR}$ chemical shifts of 10-monosubstituted nonafulvenes **1b**, **1c**, and **1d**. Plot of σ^+ [11] vs. ppm, solvent CDCl_3 .

10-Monosubstituted Nonafulvenes. According to Table 1 and Fig. 1, all the vinylic protons of nonafulvenes **1b–d** absorb in the olefinic range. While H–C(10) is affected by several factors including charge-density, anisotropy, and *van-der-Waals* effects, the nearly linear correlation of Fig. 1 has to be taken as accidental. Several effects are influencing the chemical shifts of H–C(1) and H–C(8) and even to some extent of H–C(2) as well. Of all the other protons, the chemical shifts of H–C(3), H–C(4), and H–C(6) are virtually unaffected by the exocyclic substituent, whereas H–C(7) experiences a pronounced (0.6 ppm) and H–C(5) a small (0.27 ppm) high-field shift from **1b** to **1d**. This effect is best explained as charge density effect which implies that the (*E*)-configured diene segment containing atoms C(10), C(9), C(8), C(7) is nearly planar.

Vicinal HH coupling constants of nonplanar nonafulvenes **1** should be strongly influenced by C–C bond lengths, H–C–C angles and dihedral angles. If an electron-donating substituent placed at C(10) would increase the extent of π delocalisation and reduce dihedral angles of formal single bonds, an increase of 3J of the protons adjacent to that single bond should result. On the other hand, π delocalisation of a formal double bond would reduce the vicinal H,H-coupling constant of vinylic protons. However, this effect could be counterbalanced by the decrease of H–C–C bond angles due to ring flattening.

Table 2. $^3J(H,H)$ Coupling Constants (in Hz)^{a)} of Nonafulvenes **1b–k**

Compound	$J(1,2)$	$J(7,8)$	$J(2,3)$	$J(6,7)$	$J(3,4)$	$J(5,6)$	$J(4,5)$
1b ^{b)}	12.5	13.2	2.3	4.7	12.1	12.2	^{c)}
1c ^{d)}	12.9	13.1	2.9	4.2	12.0	12.4	^{c)}
1d ^{e)}	12.00	13.05	2.73	5.27	11.82	12.28	3.03
1e ^{b)}		12.7		3.8		12.1	2.9
1f ^{f)}		12.6		3.9		12.0	2.8
1g ^{b)}		12.9		3.8		12.4	2.8
1h ^{b)}		12.6		3.8		12.3	2.7
1i ^{g)}		12.8		3.8		12.0	2.7
1k ^{h)}		13.2		4.6		12.5	3.7

a) **1d**: ± 0.02 Hz; **1b**, **1c**, and **1e–k**: ± 0.1 Hz. b) (D₆)Acetone, -40° . c) Not determined due to overlap of signals. d) CD₂Cl₂, -30° . e) CD₂Cl₂, -10° . f) (D₆)Acetone, -30° . g) CD₂Cl₂, -10° . h) CDCl₃, 0° , the equilibrium **1k** \rightleftharpoons **1k'** is mainly (but not completely) on the side of **1k**.

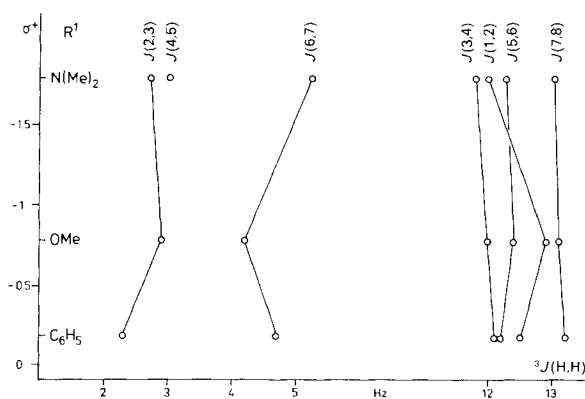


Fig. 2. Substituent effects on $^3J(H,H)$ coupling constants of nonafulvenes **1b**, **1c**, and **1d**. Plot of $\sigma^+[11]$ vs. Hz.

The most important result of Table 2 and Fig. 2 is that monosubstituted nonafulvenes contain 2 spectroscopically different ring segments. While vinylic coupling constants lying in the range of 11.8–13.2 Hz are only slightly affected by substituents R (with exception of $J(1,2)$), $J(6,7)$ is nearly 2 times as large as $J(2,3)$ and $J(4,5)$ in the spectra of nonafulvenes **1b** and **1d**. Bearing in mind the well known Karplus equation [14], the conclusion is that the dihedral angle between H–C(7), H–C(6) is comparably small, whereas the angle of the other fragments H–C(2), H–C(3) and H–C(4), H–C(5) is comparably large (near 90°). Examination of Dreiding molecular models shows that this is the case if the (*E*)-configured diene system of atoms C(7), C(8), C(9), C(10), R is nearly planar. Both coupling constants $J(2,3)$ and $J(6,7)$ are influenced by substituents and increasing from **1b** to **1d**. Although the effect is of medium size, its trend is in the right direction and might be due to a small increase in delocalisation and/or planarisation of the ring segment. According to Fig. 2, some J values of 10-methoxynonafulvene (**1c**) are surprising in so far, that $J(2,3)$ and $J(6,7)$, or $J(1,2)$ and $J(7,8)$ are approaching each other. These deviations of a nonafulvene bearing a smaller substituent could result from a higher portion of **1c''** in the equilibrium of conformers **1c'** \rightleftharpoons **1c''**.

Comparison of ^{13}C -NMR data is somewhat hampered by the fact that the ^{13}C -NMR spectrum of **1b** has not yet been assigned because 14 signals are absorbing in the narrow range of 125.2–137.5 ppm. According to Fig. 3 any change from **1b** to **1d** induces a marked high-field shift of C(9) > C(7) as well as a medium high-field shift of C(5), while C-atoms C(2), C(3), C(4), and C(6) are only slightly affected. These results confirm that charge delocalisation induced by R takes mainly place in the diene segment *trans* to the substituent R. Due to the fact that C(5) is moderately shifted to higher field, the overlap of p orbitals at C(6) and C(5) seems to be reduced but still existent in order to allow a small substituent effect at C(5).

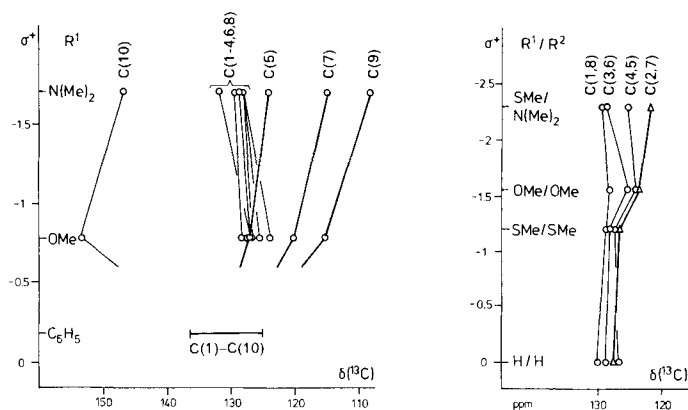


Fig. 3. Substituent effects on ^{13}C -NMR chemical shifts of nonafulvenes **1a-i**. Plot of σ^+ [11] vs. ppm; in the right-hand plot, C(9) and C(10) have been omitted due to very different steric effects of exocyclic substituents.

Finally it is important to note that ^1H - and ^{13}C -NMR chemical shifts of nonafulvenes **1b-d** are not influenced by changes of solvent polarity or temperature. For instance for the most polar nonafulvene **1d**, chemical shifts of ring protons are constant within 0.05 ppm between $+30^\circ$ and -90° (CD_2Cl_2) or within 0.07 ppm if CD_2Cl_2 is replaced by CD_3CN at -10° .

10,10-Disubstituted Nonafulvenes 1e-i. The NMR spectra of nonafulvenes **1e-h** ($\text{R}^1 = \text{R}^2$) demonstrate that pairs of ring protons as well as pairs of ring C-atoms are chemically equivalent. Similarly to **1a** [4], this is best explained by an equilibrium between 2 conformers $\mathbf{1}' \rightleftharpoons \mathbf{1}''$ which are easily transformed into each other by a switch of the exocyclic double bond. *Dreiding* molecular models suggest that this switch proceeds very easily; in fact, no line splitting or coalescence phenomena are observed in the ^1H - (400 MHz) and ^{13}C -NMR spectra (25 MHz) of **1a** or **1e-h** until -90° . The consequence of a process equilibrating nonplanar conformers $\mathbf{1}'$ and $\mathbf{1}''$ is that average values are obtained for pairs of ring protons, ring C atoms and coupling constants. Furthermore, since there exists an 1:1 population of nonafulvenes $\mathbf{1}'$ and $\mathbf{1}''$, substituent effects (e.g. on C(7,2) or $J(2,3)/J(6,7)$) should be smaller than for nonafulvenes **1b-d** and felt on both sides of the ring. According to Table 1, ^1H -NMR chemical shifts of nonafulvenes **1e-h** are typically olefinic but are not very informative with respect to electronic substituent effects. Couplings over formal single and formal double bonds are strongly alternating, and there is a good agreement between the 3J coupling constants of compounds **1e-i** and the appropriate averaged values of nonafulvenes **1b-d**.

Table 3. Selected $^4J(H,H)$ and $^5J(H,H)$ Coupling Constants (in Hz)^{a)} of Nonafulvenes **1d–k**. Solvents cf. Table 2.

Compound	$J(1,3)$	$J(2,4)$	$J(3,5)$	$J(1,4)$	$J(2,5)$
	$J(6,8)$	$J(5,7)$	$J(4,6)$	$J(5,8)$	$J(4,7)$
1d ^{b)}	1.63	1.62	1.20	0.31	2.21
	0.88	1.36	0.97	0.82	2.03
1e	± 1.3	– 2.0	– 1.2	0.5	1.9
1f	± 1.4	– 2.0	– 1.2	°)	2.0
1g	± 1.2	– 2.0	– 1.2	0.5	2.0
1h	± 1.4	– 2.1	– 1.3	0.5	2.0
1i	± 1.4	– 2.0	– 1.2	0.5	2.0
1k	± 1.2	– 1.5	– 1.1	0.6	2.1

^{a)} **1d**: ± 0.02 Hz; **1e–k**: ± 0.1 Hz. ^{b)} Sign not determined because of first-order spectrum. Further long-range couplings: [1]. ^{°)} Not determined.

For nonafulvenes **1e–1i**, some 4J and 5J coupling constants have been measured (Table 3). With exception of $J(1,3)/J(6,8)$, the sign of long-range coupling constants is strongly influencing the splitting pattern of proton signals and was, therefore, determined (Table 3). The sign of the 4J coupling constants $J(2,4)/J(5,7)$, and $J(3,5)/J(4,6)$ is negative, thus revealing a predominant π contribution. On the other hand, $J(2,5)/J(4,7)$ is remarkably large (2.0 Hz) and positive. Since σ contributions to couplings of type $^5J_{\text{het}}$ can be expected to be small, a major π contribution may be assumed which implies a good overlap of the p orbitals of the double bond with the adjacent C–H bonds. Dreiding molecular models show that this is exactly the case for $J(2,5)$ and $J(4,7)$ in both conformations **1'** and **1''**. According to Table 3, 4J as well as 5J coupling constants are not significantly influenced by exocyclic substituents.

Relatively small substituent effects are observed in the ^{13}C -NMR spectra as well, where in the series **1e**→**1i** the δ values of C(1)/C(8) and C(3)/C(6) remain nearly uninfluenced (Table 4). As for nonafulvenes **1b–d**, a significant high-field shift is observed for C(2)/C(7), however, there is no linear correlation between ^{13}C -NMR shifts and Hammett substituent constants σ^+ , especially if **1a** is included.

Table 4. ^{13}C -NMR Chemical Shifts (± 0.1 ppm, relative to TMS) of Nonafulvenes **1a–k**

Compound	C(1)	C(2)	C(3)	C(4)	C(9)	C(10)
	C(8)	C(7)	C(6)	C(5)		
1a ^{a)}	130.4	127.2	128.7	126.7	143.5	122.0
1c ^{b)}	123.9	°)	128.1	125.4	115.3	153.4
	°)	121.2	127.1	°)		
1d ^{d)}	127.8	127.7	129.2	127.7	108.3	146.7
	131.9	115.1	128.6	124.1		
1e ^{e)}	128.4	127.1	128.1	127.2	137.4	140.0
1f ^{f)}	127.9	124.6	127.9	126.6	122.2	143.4
1g ^{g)}	128.2	123.8	125.6	124.0	99.8	158.7
1h ^{h)}	127.8	121.2	125.0	123.2	84.0	160.8
1i ⁱ⁾	129.2	121.7	128.7	125.4	117.2	154.6
1k ^{j)}	128.1	114.4	127.2	122.8	94.8	164.2

^{a)} (D_6)Acetone, –30°. ^{b)} CD_2Cl_2 , –30°. ^{c)} One of 3 signals at 128.7, 126.8 and 126.5 ppm. ^{d)} CDCl_3 , –10°. ^{e)} CDCl_3 , –25°. ^{f)} CDCl_3 , –30°. ^{g)} CDCl_3 , –40°. ^{h)} CD_2Cl_2 , –60°. ⁱ⁾ CDCl_3 , 0°, the equilibrium **1k**⇌**1k**[±] is mainly (but not completely) on the side of **1k**.

According to the results summarised in *Tables 1* and *4*, nonafulvenes **1e–h** are similar in behaviour to nonafulvene **1a** itself. As for monosubstituted nonafulvenes **1b–d**, electronic effects of exocyclic substituents are observed in the nearly planar ring segment, but obviously averaged due to a fast conformational process. In agreement with **1a** as well as with **1b–d**, ¹H-NMR chemical shifts of nonafulvenes **1e–h** are not influenced by changes of solvent polarity or temperature in the range of + 30° to – 90° (*Table 5*).

Table 5. Influence of Temperature and Solvent on Chemical Shifts of 10,10-(1,2-Ethylenedithio)nonafulvene (**1f**)

Solvent	Temperature	H–C(1,8)	H–C(2,7)	H–C(3,6)	H–C(4,5)
CD ₂ Cl ₂	+ 30°	6.10	5.64	6.04	5.86
CD ₂ Cl ₂	0°	6.09	5.63	6.04	5.86
CD ₂ Cl ₂	– 30°	6.09	5.63	6.04	5.85
CD ₂ Cl ₂	– 60°	6.08	5.62	6.04	5.85
CD ₂ Cl ₂	– 90°	6.06	5.60	6.03	5.84
CD ₃ COCD ₃	– 30°	6.05	5.58	5.99	5.81

The same results are obtained for 10-(dimethylamino)-10-methylthiononafulvene (**1i**), whose ¹H-NMR chemical shifts are constant in a δ range of ± 0.06 ppm between – 10° and – 90° or in solvents like CD₃CN, (CD₃)₂CO, or CD₂Cl₂. Moreover, **1i** perfectly fits into the series of nonafulvenes **1e–h** with respect to ¹H- and ¹³C-NMR shifts as well as H,H-coupling constants (*Tables 1–5*). However, in contrast to expectations, pairs of ring C-atoms and ring protons of **1i** are equivalent in the temperature range of + 20° to – 40°, and a set of average coupling constants is resulting from spectral analysis. Below – 60°, coalescence phenomena are observed for H–C(1)/H–C(8) in the 400-MHz ¹H-NMR spectra as well as for ring C-atoms and *N*-CH₃ groups in the 25-MHz ¹³C-NMR spectra. At – 88°, separate broad signals are observed for C(2) and C(7) as well as for the *N*-CH₃ groups [15]. Coalescence of the *N*-CH₃ groups is easily explained by a hindered rotation around the C–N bond, a process well known for 6-(dimethylamino)pentafulvene as well [16]. Due to the fact that splitting of pairs of ring protons and ring C-atoms of **1i** takes place at very low temperature, rotation around the exocyclic double bond²⁾ is surprisingly fast for **1i** compared with 6-(dimethylamino)pentafulvene (**4d**), for which a ΔG^\ddagger value of 22 kcal/mol has been measured in DMSO [17]. We are planning to investigate the behaviour of **1i** in more detail.

10,10-Bis(dialkylamino)nonafulvenes **1j** and **1k**. In clear contrast to nonafulvenes **1a** and **1b–i**, chemical shifts and H,H-coupling constants of nonafulvenes **1j** and **1k** [3] [6] are strongly influenced by changes in temperature and/or solvent polarity. Because of more pronounced effects and better resolved spectra, some new experiments with **1k** completing previous findings of *Hafner* and *Tappe* [3] [6] are reported.

In CDCl₃ solution at 0°, chemical shifts and H,H-coupling constants of 10,10-bis(dimethylamino)nonafulvene (**1k**) are very similar to those of nonafulvenes **1b–i** (*cf. Tables 1–5*). Substituent effects are observed in the expected direction, influencing H–C(2)/H–C(7) and C(9) > C(2)/C(7) > C(4)/C(5), and vicinal coupling constants are strongly

²⁾ Rotation around the exocyclic double bond (C(9)=C(10)) of nonafulvenes is supposed to be a rather complex process, which is not known in detail so far. It may be assumed that the ease of rotation increases with increasing electron-donating capacity of the substituents R¹ and R², and that means, with increasing π delocalization and planarization of the segment involved in the process.

alternating. According to the NMR analysis of nonafulvenes **1b–i** reported here, these results show that in CDCl_3 at 0° **1k** behaves like an olefinic molecule with a nine-membered ring strongly deviating from planarity; substituent effects are in agreement with a conformational equilibrium of the type $\mathbf{1k} \rightleftharpoons \mathbf{1k}'$.

Fig. 4–6 demonstrate the pronounced effect of temperature and solvent polarity on ^1H - and ^{13}C -NMR chemical shifts as well as on vicinal H,H-coupling constants of **1k**. If the temperature of CD_2Cl_2 solutions is gradually reduced from $+30^\circ$ to -90° , then the signals of the vinylic ring protons of **1k** are shifted from the olefinic range (6.32–5.59 ppm) to the aromatic range of the spectrum (7.24–6.92 ppm, *Fig. 4*). Similarly to **1j**, the strongest effect ($\Delta\delta = 1.51$ ppm) is observed for H–C(2)/H–C(7). A similar although somewhat reduced effect is observed if CDCl_3 is gradually replaced by CD_2Cl_2 , $(\text{CD}_3)_2\text{CO}$, and CD_3CN [6]. Solvent- and temperature-dependent ^1H -NMR chemical shifts of that

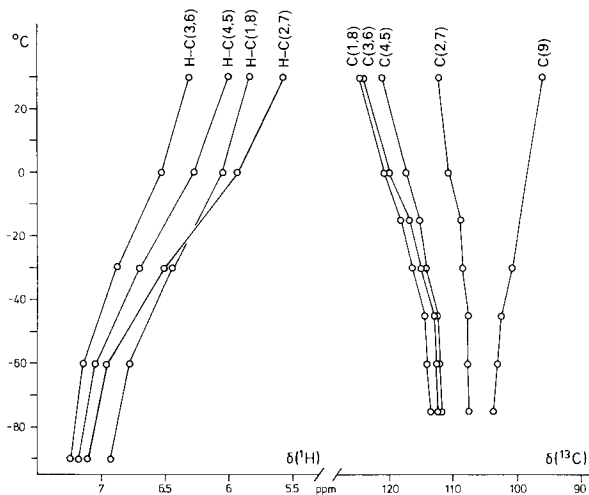


Fig. 4. Influence of temperature on ^1H - and ^{13}C -NMR chemical shifts of 10,10-bis(dimethylamino)nonafulvene (**1k**). Plot of $^\circ\text{C}$ vs. ppm, solvent: CD_2Cl_2 .

magnitude could tentatively be explained by an equilibrium between the olefinic nonafulvene **1k**, dominating in unpolar solvents and/or at ambient temperature, and an aromatic species, dominating in polar solvents and/or at low temperature. The most reasonable aromatic species inducing a ring current is the amidino-cyclononatetraenide $\mathbf{1k}^\pm$. In fact, an equilibrium $\mathbf{1k} \rightleftharpoons \mathbf{1k}^\pm$ would explain the ^1H -NMR data of **1k**: with increasing concentration of $\mathbf{1k}^\pm$, protons would feel the *ring current effect of the aromatic 10π system* which should be reduced to some extent by the negative charge of the delocalised cyclononatetraenide.

Since ^{13}C -NMR shifts are not influenced by ring current effects, an increasing negative charge of C-atoms is expected to produce a considerable *high-field shift of ^{13}C -NMR signals*, which is in fact observed for C(2) to C(8) (*Fig. 4*). The effect is most pronounced for C(1)/C(8) and C(3)/C(6), decreasing for C(4)/C(5), C(2)/C(7) and counterbalanced for C(9). This is reasonably explained if one takes into account substituent effects operating in the olefinic nonafulvene **1k** and inducing some amount of negative charge on

$C(9) > C(2)/C(7) > C(4)/C(5)$. If delocalisation produces a nearly equal charge distribution for each C atom of $1\mathbf{k}^\pm$, then the increase in negative charge (going from $1\mathbf{k}$ to $1\mathbf{k}^\pm$) should be most pronounced for C(1)/C(8) and C(3)/C(6) and decrease in the series $C(4)/C(5) > C(2)/C(7) > C(9)$. According to Fig. 4, the expected trend is confirmed by the experimental results. As far as C(9) is concerned, the comparably small charge-density effect seems to be outweighed by another effect resulting in an overall low-field shift. A low-field shift of C(9) may be expected if the change from $1\mathbf{k}$ to $1\mathbf{k}^\pm$ is not only accompanied by a planarisation of the nine-membered ring, but an arrangement of the exocyclic substituent out of plane of the cyclononatetraenide unit. In this case, charge separation between C(9) and C(10) should result and induce a pronounced low-field shift of C(10) as well, which is in fact observed ($\Delta\delta = 20.6$ ppm between 0 and -75° in CD_2Cl_2).

Lowering temperature or replacing unpolar solvents by polar solvents has a very strong influence on the $^3J_{H,H}$ -coupling constants of $1\mathbf{k}$ (Fig. 5 and 6). $J(2,3)/J(6,7)$ and $J(4,5)$ are increasing from 4.6 and 3.7 Hz in $CDCl_3/0^\circ$ to 7.2 and 6.9 Hz in $CD_2Cl_2/0^\circ$, and to 10.7 and 9.5 Hz in $CD_3CN/0^\circ$. In CD_2Cl_2 solution at -90° , values of 12.4 and 11.9 Hz

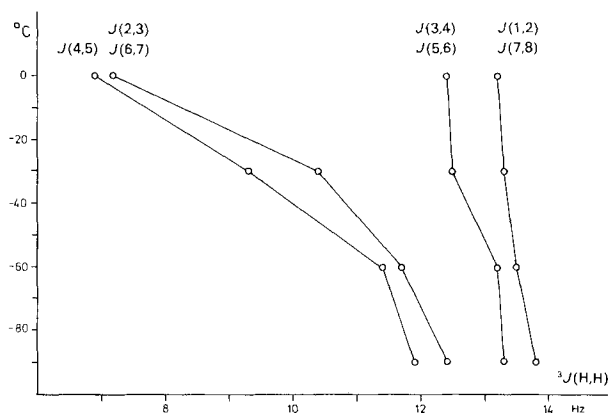


Fig. 5. Influence of temperature on $^3J(H,H)$ coupling constants of $1\mathbf{k}$. Plot of $^\circ C$ vs. Hz, solvent: CD_2Cl_2 .

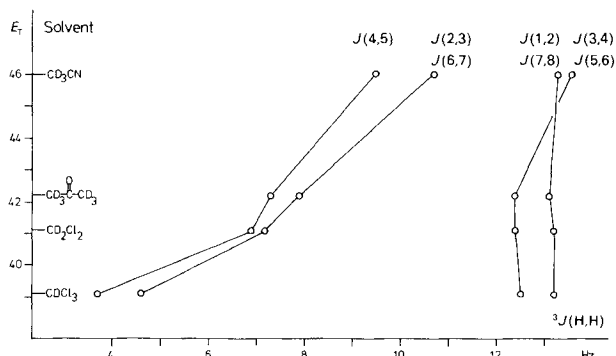


Fig. 6. Influence of solvents on $^3J(H,H)$ coupling constants of $1\mathbf{k}$. Plot of E_T values [18] vs. Hz, 0° .

are observed which are nearly of the same magnitude as $J(1,2)/J(7,8) = 13.8$ Hz and $J(3,4)/J(5,6) = 13.3$ Hz. This dramatic change may convincingly be explained by planarisation of the cyclononatetraene unit as well as by π delocalisation. Once again, coupling constants over formal double bonds are virtually not influenced by temperature or solvent polarity. Bearing in mind the well known influence of H–C–C bond angles on 3J coupling constants [19], a tentative argument is that this effect could counterbalance the expected decrease of 3J values due to delocalisation.

Summarising, the NMR results presented here are in good agreement with an equilibrium of the type $\mathbf{1k} \rightleftharpoons \mathbf{1k}^\pm$ as suggested by *Boche* [7]: in unpolar solvents and at ambient temperature, chemical shifts and coupling constants as well as substituent effects of $\mathbf{1k}$ are very similar to those of olefinic nonafulvenes $\mathbf{1a-h}$. On the other hand, the NMR spectra measured in CD_2Cl_2 solution at -80° to -90° are consistent with a dipolar amidino-cyclononatetraenide $\mathbf{1k}^\pm$. Whereas the ^{13}C -NMR shifts suggest an increase of negative charge of the ring C-atoms, the low-field shift of ring protons seems to be due to the ring-current effect of the cyclononatetraenide unit, and the pronounced increase of 3J coupling constants of formal single bonds reflects an increasing ring flattening and π delocalisation.

Closing Remarks. Nonafulvenes investigated so far may be classified into three categories: 1) Nonafulvenes $\mathbf{1a-h}$ are olefinic molecules with alternating bond lengths, their nine-membered ring deviating strongly from planarity. The 10-monosubstituted nonafulvenes $\mathbf{1b-d}$ have two sterically very different ring segments with a nearly planar (*E*)-diene system (consisting of C(7), C(8), C(9), C(10), and R); electron-donating substituents R are influencing $\text{C}(9) > \text{C}(7) > \text{C}(5)$. A fast process is equilibrating conformers $\mathbf{1}'$ and $\mathbf{1}''$ so that pairs of ring C-atoms are equivalent and only average substituent effects are observed for $\text{C}(9) > \text{C}(2)/\text{C}(7)$ in symmetrically substituted nonafulvenes $\mathbf{1e-h}$ compared with $\mathbf{1a}$. ^1H - and ^{13}C -NMR spectra are not influenced by temperature and solvent polarity, and no coalescence phenomena are observed between 0 and -100° . 2) Nonafulvene $\mathbf{1i}$ is an olefinic nonplanar molecule completing the series $\mathbf{1a-h}$ at the polar side and showing no influence of temperature and solvent polarity on chemical shifts. However, rotation around the exocyclic double bond²⁾ is fast enough so that pairs of ring C atoms and ring protons are equivalent above -50° . 3) The spectroscopic data of nonafulvenes $\mathbf{1j}$ and $\mathbf{1k}$ are in good agreement with an equilibrium of the type $\mathbf{1k} \rightleftharpoons \mathbf{1k}^\pm$ [7] which is strongly influenced by changes of solvent and temperature. The results presented here do not allow a complete analysis of all the effects influencing equilibria of type $\mathbf{1k} \rightleftharpoons \mathbf{1k}^\pm$. However, they are in good agreement with the model proposed by *Boche* [7] and even allow a generalisation to all the nonafulvenes $\mathbf{1a-k}$ studied so far (further tentative explanations have been discussed by *Sabbioni* [15]). Obviously unpolar nonafulvenes of type A (like $\mathbf{1a}$ and $\mathbf{1b}$) are characterised by a high free energy of the dipolar forms $\mathbf{1a}^\pm$ and $\mathbf{1b}^\pm$ which implies a high free activation energy ΔG^\ddagger of the rotation around the exocyclic double bond²⁾. Similarly to pentafulvenes [16], it may be assumed that ΔG^\ddagger of rotation is considerably lowered by electron donating substituents R^1 and R^2 . This means that the free energy of the dipolar intermediate $\mathbf{1}^\pm$ is more strongly influenced by substituents than the free energy of the fulvenic conformers $\mathbf{1}$.

For fulvenes of type B rotation around $\text{C}(9)=\text{C}(10)$ ²⁾ is fast enough so that ^1H -NMR spectra of the type $AA'MM'XX'YY'$ are observed at ambient temperature. However, as long as the dipolar form $\mathbf{1}^\pm$ is still high enough in free energy, solvent and temperature

effects favouring 1^{\pm} do not allow any measurable population of the intermediate so that no effects on NMR chemical shifts are observed.

Very obviously *nonafulvenes* **1j** and **1k** are of *type C*: it seems that at ambient temperature and in unpolar solvents the dipolar forms $1j^{\pm}$ and $1k^{\pm}$ are only some kcal/mol higher in free energy than the fulvenic forms **1j** and **1k** so that NMR chemical shifts and coupling constants are comparable to those of the series **1a–i**. With increasing solvent polarity the dipolar form is increasingly stabilised by solvation. As soon as populations of $1j^{\pm}$ and $1k^{\pm}$ are increasing, NMR spectra are strongly influenced by solvents. Since solvation produces some complexation of solvent molecules, any change of the type $1k^{\pm} + x \cdot \text{solvent} \rightarrow 1k^{\pm}(\text{solvent})_x$ is accompanied by an increase in order and a decrease in entropy. Consequently, the strong influence of temperature on the spectra of **1j** and **1k** is reasonably explained as an entropy effect. In fact, processes like $3 \rightarrow 3^{\pm}$ ($\Delta H = -7$ kcal/mol, $\Delta S = -30$ cal/° · mol [7]) and $1k \rightarrow 1k^{\pm}$ ($\Delta H \approx -6.5$ kcal/mol, $\Delta S \approx -22$ cal/° · mol, as roughly estimated from UV data [6]) are moderately exothermic so that the dipolar forms are predominant at low temperature where the entropy term is small. This term is dominating the equilibrium at high temperature so that the fulvenic forms are becoming important.

Finally, it has to be noted that a further increase of the electron-donating power of R^1 and R^2 could stabilise the dipolar forms 1^{\pm} to an extent that *nonafulvenes of type D* would exclusively exist as carbeno-cyclononatetraenides 1^{\pm} ; *nonafulvenes of this type* are unknown so far.

The NMR-spectroscopic behaviour of all the *nonafulvenes* isolated so far [2] [3] [8] [9] is reasonably explained by the qualitative scheme of *Fig. 7*, which is based on a model proposed by *Boche* [7] for equilibria of the type $1k \rightleftharpoons 1k^{\pm}$. In view of a more detailed understanding of the conformational behaviour of *nonafulvenes*, theoretical calculations of the effects influencing these equilibria with respect to various substituents and conformers are indispensable. Synthetic attempts towards new *nonafulvenes*, especially of *type D*, would be very useful. New spectroscopic results giving more precise informations

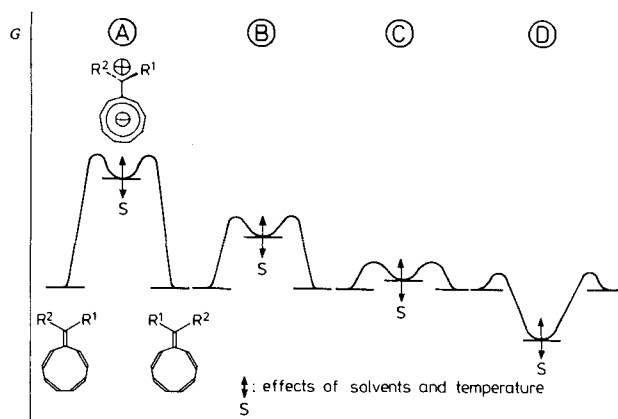


Fig. 7. Schematic representation of different types of *nonafulvenes* in dependence of the difference in free energy ΔG between the nonplanar *nonafulvenes* **1** and the dipolar carbeno-cyclononatetraenide 1^{\pm} . A–D: type of *nonafulvene*, see text.

about substituent effects on the extent of π delocalisation as well as planarisation of the fulvene ring are required. Furthermore, a complete NMR analysis of the system $3 \rightleftharpoons 3^+$ [7] could definitely confirm the close similarities between nonafulvenolates **3** and nonafulvenes **1**.

Experimental Part

Nonafulvenes **1a** [4], **1b**, **1c** [9], **1d** [8], **1e–1j** [9] and **1k** [3] [6] (for an improved procedure of **1k** cf. [9]) have been prepared by literature methods. ^1H - and ^{13}C -NMR spectra were recorded on Bruker WH-400, WM-400, and AM-400 instruments and a Varian XL-100 spectrometer in solvents and temp. given in Tables 1–5. NMR-sampling techniques used for instable nonafulvenes and strategies applied to the analysis of ^1H -NMR spectra of **1b**, **1c**, and **1d** are identical with those described in [1] for **1d**.

For the analysis of $AA'MM'XX'YY'$ spectra of nonafulvenes **1e–k** a first set of ^1H -NMR chemical shifts and H,H-coupling constants was obtained by approximate analysis, decoupling, and NO experiments and comparison with J values of 10-monosubstituted nonafulvenes [1]. Because of the high-order appearance of the 400-MHz spectra, simulations of subsystems [1] were useless. Simulation and iteration of the 8-spin systems was performed on a computer of the type Aspect 2000 using the Bruker Panic program [20].

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