

17. NMR-Spectroscopic Investigations of Potentially Planarized Nonafulvenes¹⁾

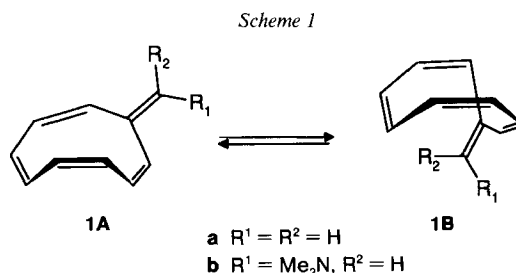
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¹H- and ¹³C-NMR spectra of nonafulvene **1e** and nonafulvenes **2** and **3** have been assigned, high-resolution ¹H-NMR spectra of **2** (600 MHz, Fig. 3) and of **3** (400 MHz, Fig. 2) have been analyzed, and the data are compared with those of other nonafulvenes (Tables 1–6). Generally speaking, according to their spectroscopic behavior, four classes of nonafulvenes (A–D) may be distinguished (Fig. 1). The investigation shows that compounds **1e** and **3** belong to class A, being characterized by ¹H-chemical shifts around 6 ppm, strongly alternating ³J(H,H) and ¹³C chemical shifts in the range of 123 to 130 ppm, thus existing in the olefinic form with a non-planar nine-membered ring. On the other hand, **2** is the first nonafulvene of class D, being characterized by ¹H chemical shifts in the aromatic range, large ³J(H,H) values of the same size, and ¹³C chemical shifts around 110 ppm. Since NMR parameters are virtually not influenced by temperature (–50° to 50°) or solvents, it is concluded that **2** exclusively exists in the dipolar structure **2[±]** with a planarized nine-membered ring. According to Fig. 4, these classes (and their spectroscopic data) are linked by 10,10-bis(dimethylamino)nonafulvene (**1c**; and its temperature-dependent NMR parameters): for **1c**, a temperature-dependent equilibrium $\mathbf{1c} \rightleftharpoons \mathbf{1c}^{\pm}$ had earlier been established.

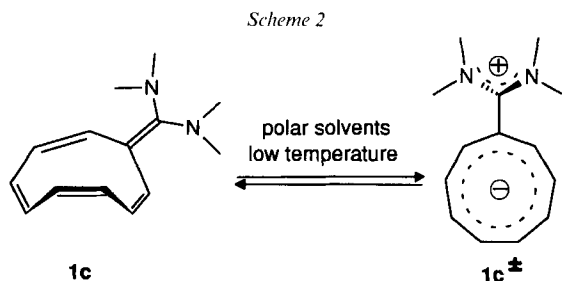
1. Introduction. – Nonafulvenes are cross-conjugated molecules with a nine-membered ring. UV- and NMR-spectroscopic investigations show that parent nonafulvene **1a** is a typically non-planar olefinic molecule [3]. The fact that pairs of ring protons and ring C-atoms are equivalent indicates an easy switch of the exocyclic C=C bond $\mathbf{1A} \rightleftharpoons \mathbf{1B}$ (Scheme 1) by which diastereotopic ring segments are transformed into each other. These ring segments may be distinguished in 10-monosubstituted nonafulvenes such as 10-(dimethylamino)nonafulvene **1b** ($R^1 = \text{Me}_2\text{N}$, $R^2 = \text{H}$) for which the equilibrium $\mathbf{1A} \rightleftharpoons \mathbf{1B}$ is totally shifted towards **1A** [4]. With one exception, all the nonafulvenes prepared so far²⁾ are non-planar olefinic molecules and do not show any dependence of ¹H and ¹³C chemical shifts, or of coupling constants on temperature or solvent polarity.



¹⁾ Fulvenes, Fulvalenes, Part 68; Part 67: [1]. Part 66 (short communication): [2].

²⁾ For surveys see [5–7].

The exception is 10,10-bis(dimethylamino)nonafulvene (**1c**; Scheme 2) [8] whose spectacular NMR-spectroscopic behavior has first been observed by *Hafner* and *Tappe* [9] [10], explained by *Boche et al.* [11]³⁾ and finally established by our NMR investigations [4] [12]:



At room temperature and in unpolar solvents, **1c** displays the features which are typical for **1a**, **1b**, and other unpolar nonafulvenes: ¹H chemical shifts are in the olefinic range, ³J values are strongly alternating, and ring C-atoms C(1) to C(8) absorb around 120 ppm. Lowering temperature (or increasing solvent polarity) has a dramatic effect on all the NMR parameters of **1c**: ring protons experience a low-field shift from the olefinic to the aromatic range; ³J values over formal single bonds strongly increase and approach ³J values over formal double bonds, and ring C-atoms C(1)–C(8) undergo a high-field shift of at *ca.* 12 ppm. These results perfectly agree with the expected properties of dipolar structure **1c**[±] being characterized by a planarized nine-membered ring; **1c**[±] is thought to be stabilized by polar solvents (solvation) and at low temperature (due to a negative reaction entropy⁴⁾). Thus, **1c** behaves very similarly to sodium nonafulvenolates [11]⁴⁾ (*Fig. 1*).

If all the nonafulvenes prepared so far are examined, then three classes of nonafulvenes may be distinguished: type-*A* nonafulvenes with relatively weakly electron-donating substituents exist in the non-planar olefinic form; the energy of the corresponding carbeno-cyclononatetraenide **1**[±] will be high, as well as the activation energy for rotation around the exocyclic C=C bond. With increasing electron-donating capacity of the substituents, the energy of the dipolar intermediate **1**[±] will be lowered, so that the activation energy for a rotation around the exocyclic C=C bond is supposed to be smaller as well. This case is observed for **1d**, where pairs of ring protons and ring C-atoms are NMR-spectroscopically equivalent at room temperature (type-*B* nonafulvenes). **1c** is the exponent of type-*C* nonafulvenes, in which the energy of the non-planar olefinic form **1c** is so close to the level of the dipolar form **1c**[±] that solvent or temperature effects will favor either **1c** or **1c**[±].

Finally, a so far unknown class-*D* of nonafulvenes may be foreseen in which the dipolar form **1**[±] will be much lower in energy than the nonafulvene form. Nonafulvenes of that type would be characterized by a planar (or nearly planar) nine-membered ring

³⁾ An early explanation given by *Hafner* [10] had to be abandoned in the light of new NMR experiments [12].

⁴⁾ UV Extrapolations [9] suggest $\Delta H^\circ = -6.5 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\circ = -22 \text{ eu}$ for the process **1c** → **1c**[±]. Similarly, *Boche et al.* [11] determined $\Delta H^\circ = -6.9 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\circ = -30 \text{ eu}$ for the equilibrium between sodium 10-methylnonafulven-10-olate and sodium acetylcyclononatetraenide.

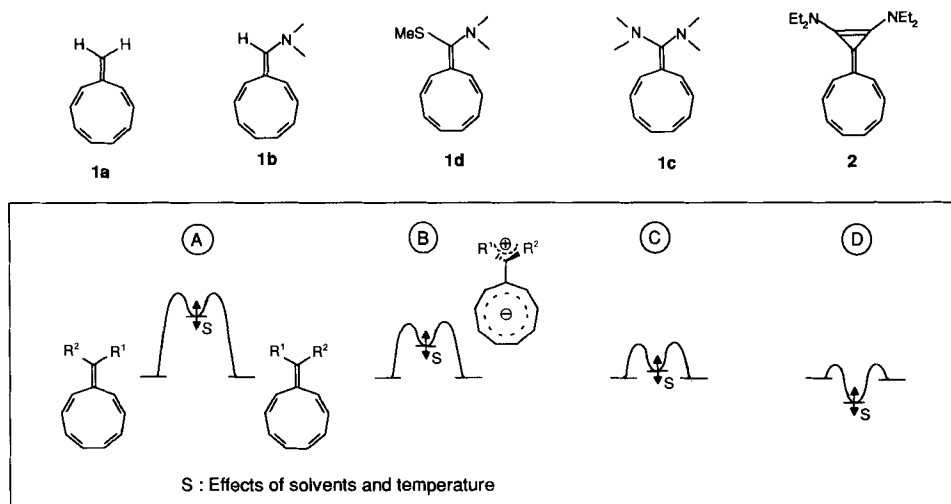
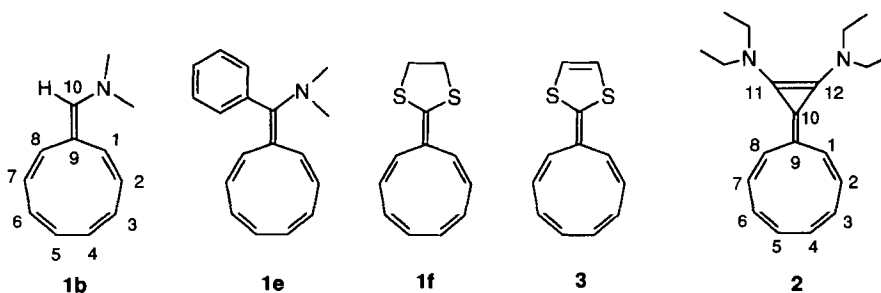


Fig. 1. Classes A, B, C, and D of nonafulvenes dependent on the differences in free energy ΔG between the non-planar nonafulvenes **1** and the dipolar carbene-cyclononatetraenide, and typical examples for each class⁵⁾

and, therefore, a nearly complete π delocalization. Furthermore, the dipolar form is expected to be predominant at ambient temperature as well.

In a recent synthetic attempt towards nonafulvenes of class *D*, we were successful in isolating, besides model compound **1e**, 11,14-dithianonapentafulvene (**3**) and 11,12-bis(dimethylamino)nonatriafulvalene (**2**) [1]. In this paper, we will discuss the NMR results of these novel compounds.



2. Assignment and Analysis of NMR Spectra⁶⁾. – Due to the fact that a considerable number of ¹H-NMR spectra of nonafulvenes have already been analyzed [3] [4] [12], a first assignment of ¹H-NMR signals is normally made by comparison of the splitting pattern with that of a similarly substituted compound. So, the signals of **1e** are easily

⁵⁾ The spectroscopic results presented in this paper (see later) clearly demonstrate that **2** is the first nonafulvene of class *D*.

⁶⁾ For details of the applied procedures, see *Exper. Part* and [13].

assigned by comparison with **1b** [4], while those of nonafulvene **3** are assigned by comparison with **1f** [12]. These assignments are then confirmed by usual techniques like *COSY*, decoupling experiments, and NOE experiments⁷⁾.

The analysis of the ¹H-NMR spectrum of 10-(dimethylamino)-10-phenylnonafulvene (**1e**) was based on the complete analysis of 10-(dimethylamino)nonafulvene (**1b**) which displays an approximate first-order spectrum at 400 MHz. However, due to signal overlap, the spectrum of **1e** is much more complex. An approximate analysis resulted by simulating the spectrum of **1e** with the values of the coupling constants obtained from **1b**, followed by adjusting these values by comparison of simulated and experimental spectra.

Analysis of the ¹H-NMR spectrum of 11,14-dithianonapentafulvalene (**3**) would normally be expected to be much more complicated than that of **1e** due to its *AA'MM'XX'YY'* character. However, since **3** turned out to be an unpolar nonafulvene with chemical shifts and coupling constants very similar to those of nonafulvene **1f** (see later), simulation of the spectrum of **3** with approximate δ values of **3** and the complete set of *J* values of **1f** gave a surprisingly good first approximation. After assignment of 52% of the theoretical transitions, iteration resulted in the spectrum given in Fig. 2.

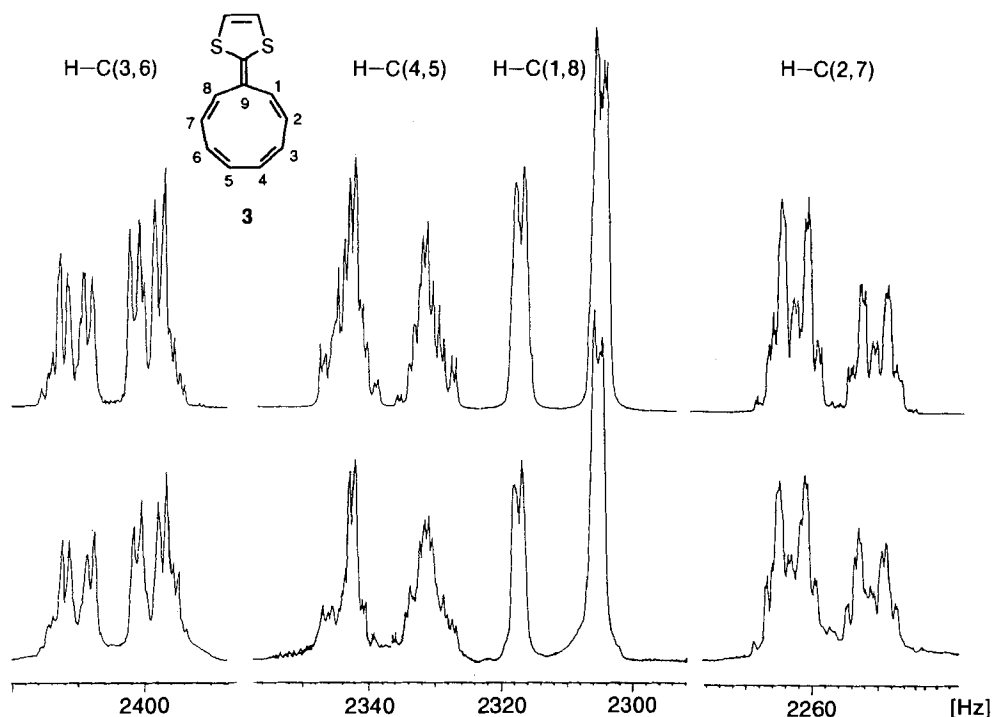


Fig. 2. Sections of the 400-MHz ¹H-NMR spectrum of **3** (CD₂Cl₂, 10°): experimental spectrum (below) and multiplets after simulation and iteration (above)

⁷⁾ NOE Experiments are crucial for distinguishing H-C(1) and H-C(8) (showing a nearly identical splitting) of unsymmetrically substituted nonafulvenes such as **1b** [4] and **1e**.

Much more problems were encountered in the $^1\text{H-NMR}$ analysis of *11,12-bis(diethylamino)nonatriafulvalene* (**2**). First of all, a rough inspection of the experimental spectrum (Fig. 3, lower trace) showed that δ and J values strongly differed from those of unpolar nonafulvenes. Although H–C(1)/H–C(8) could be easily assigned to the high-frequency doublet and H–C(2)/H–C(7) to the approximate doublet of doublets at low frequency, protons H–C(3) to H–C(6) were extremely complex at 400 MHz and were still overlapping at 600 MHz (Fig. 3). Furthermore, it was surprising to see that the number of observed lines of this $AA'BB'XX'YY'$ -type spectrum was considerably smaller than that of the $AA'MM'XX'YY'$ -type spectrum of **3** which hinted at the conclusion that a lot of long-range couplings would be very small. Finally, the splitting pattern of the low-frequency dd of H–C(2)/H–C(7) showed that $J(2,3)/J(6,7)$ were nearly as large as $J(1,2)/J(7,8)$. This prompted us to try a first simulation with roughly approximate experimental δ values together with 3J values of the -90° $^1\text{H-NMR}$ spectrum of dipolar 1c^\ominus ([8] [9]) analyzed earlier [12] [14] which was surprisingly similar to that of **2**. Simulations/iterations⁶ gave, after a stepwise introduction of small 4J values, a good fit with the experimental spectrum (Fig. 3).

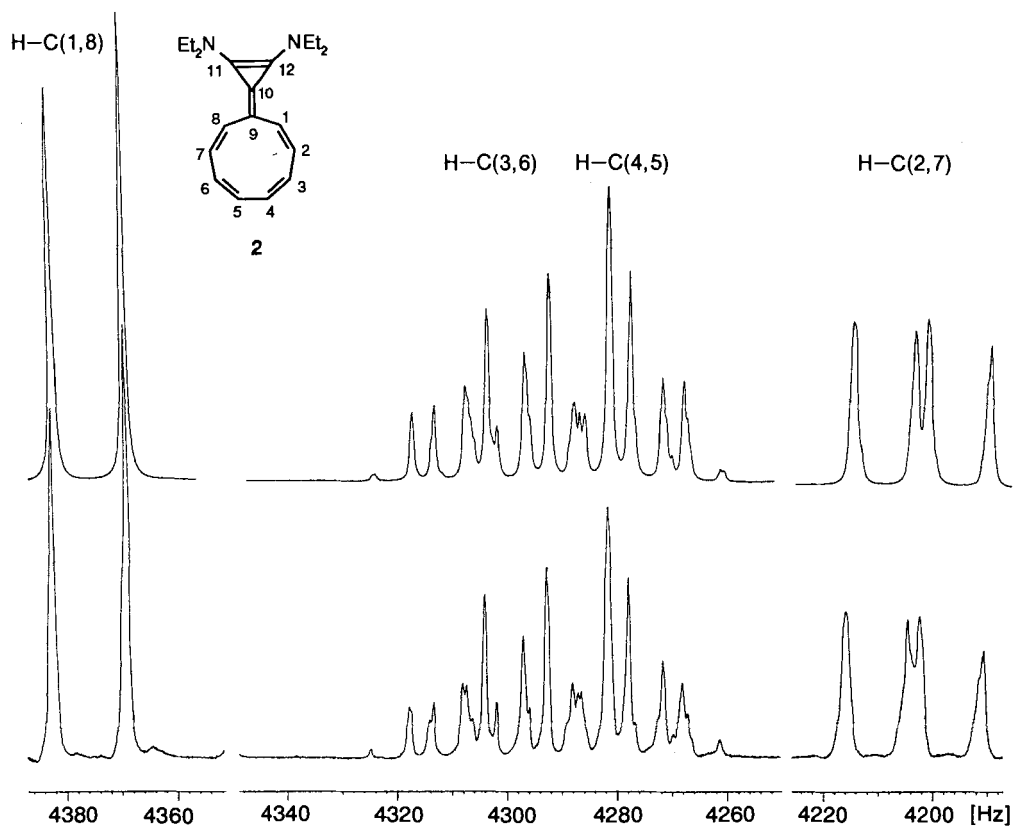


Fig. 3. Sections of the 600-MHz $^1\text{H-NMR}$ spectrum of **2** (CDCl_3 , r.t.): experimental spectrum (below) and multiplets after simulation and iteration (above)

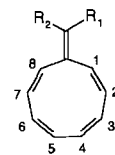
Sets of ^1H chemical shifts, of coupling constants as well as of ^{13}C chemical shifts, of nonafulvene **1c**, and nonafulvenes **2** and **3** together with reference compounds **1b** and **1f** are listed in *Tables 1–6*⁸⁾.

Table 1. ^1H Chemical Shifts (ppm, relative to TMS) of Nonafulvenes **1b** [4], **1e**, **1f** [12], and of Nonafulvenes **2** and **3** (400 or 600 MHz [13])

H-Atom	1b ($\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{H}$) ^{a)}	1e ($\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{Ph}$) ^{a)}	1f ^{b)}	3 ^{c)}	2 ^{d)}
H–C(1)	6.26	6.23	6.00	6.12	7.29
H–C(8)	5.61	5.78			
H–C(2)	5.76	5.75	5.50	5.64	7.00
H–C(7)	4.92	5.24			
H–C(3)	6.02	6.14	6.08	6.05	7.17
H–C(6)	5.82	6.03			
H–C(4)	5.92	5.87	5.81	5.85	7.12
H–C(5)	5.45	5.75			
H–C(10)	6.00	–	–	–	–

^{a)} (D_6)Acetone, -10° , shifts very similar in CDCl_3 . ^{b)} CDCl_3 , -30° . ^{c)} CD_2Cl_2 , 10° . ^{d)} CDCl_3 , r.t.

Table 2. 3J , 4J , and Important ($> 1 \text{ Hz}$) 5J Values (in Hz) of Nonafulvene **1b** [4]^{a)}^{b)} as well as of Nonafulvenes **2** and **3** [13]



J	1b ($\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{H}$) ^{b)} ^{c)}	3	2
$J(1,2)$	12.0	12.5	13.6
$J(7,8)$	13.1		
$J(2,3)$	2.7	4.0	11.8
$J(6,7)$	5.3		
$J(3,4)$	11.8	12.0	13.2
$J(5,6)$	12.3		
$J(4,5)$	3.0	3.0	11.7
$J(1,3)$	± 1.6	± 1.3	0.1
$J(6,8)$	± 0.9		
$J(2,4)$	± 1.6	± 1.5	0.2
$J(5,7)$	± 1.4		
$J(3,5)$	$\bullet 1.2$	± 1.1	0.2
$J(4,6)$	± 1.0		
$J(1,8)$	± 0.4	± 0.4	0.2
$J(2,5)$	2.2	2.1	d)
$J(4,7)$	2.0		

^{a)} All coupling constants of **1e** are very similar to those of **1b** [13], however, the data of fully analyzed **1b** are more reliable. ^{b)} Most 4J couplings of **1b** are supposed to be negative; however, due to the first-order type of the spectrum, the sign could not be determined. ^{c)} For more small long-range couplings of fully analyzed **1b**, see [4]. ^{d)} Very small, probably $< 0.1 \text{ Hz}$.

⁸⁾ Assignments of ^{13}C -NMR spectra were confirmed by ^{13}C , ^1H -correlated 2D spectra.

Table 3. ^{13}C Chemical Shifts (ppm, rel. to TMS) of the Nonfulvene Units of **1b** [4], **1e**, **1f** [12], **2**, and **3**

C-Atom	1b ($\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{H}$) ^{a)}		1e ($\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{Ph}$) ^{b)}		1f ^{c)}	3 ^{d)}	2 ^{e)}
C(1)	127.8	} 129.8	128.9	} 130.0	127.9	127.0	113.5
C(8)	131.9		131.1				
C(2)	127.7	} 121.4	126.0	} 123.8	124.6	125.3	107.4
C(7)	115.1		121.7				
C(3)	129.2	} 128.9	128.9	} 128.9	127.9	128.1	113.2
C(6)	128.6		128.9				
C(4)	127.7	} 125.9	126.9	} 125.9	126.6	127.4	112.4
C(5)	124.1		124.9				
C(9)	108.3	108.3	117.9	117.9	122.2	118.1	97.8
C(10)	146.7	146.7	138.5	138.5	143.4	141.4	128.7

^{a)} CDCl_3 , -10° . ^{b)} CD_2Cl_2 , -25° . ^{c)} CDCl_3 , -30° . ^{d)} CDCl_3 , -10° . ^{e)} CDCl_3 , 0° .

Table 4. Temperature Dependence of ^1H Chemical Shifts (CD_2Cl_2) as well as of ^{13}C Chemical Shifts (CDCl_3) of **3**

Temp. [$^\circ\text{C}$]	H–C(1,8)	H–C(2,7)	H–C(3,6)	H–C(4,5)	C(1,8)	C(2,7)	C(3,6)	C(4,5)
+ 24	5.79	5.65	6.02	5.85	127.3	125.5	128.2	127.5
+ 10	5.77	5.64	6.01	5.84	127.2	125.5	128.2	127.6
– 10	5.75	5.63	6.00	5.83	127.0	125.3	128.1	127.4
– 40	5.74	5.62	6.00	5.83	126.7	124.6	127.7	126.8
– 60	5.73	5.61	5.99	5.83	126.5	124.6	127.7	126.8
$\Delta\delta_{\text{max}}$ [ppm] ^{a)}	0.06	0.04	0.03	0.02	0.8	0.9	0.5	0.7

^{a)} Maximum shift difference relative to δ values at r.t.

Table 5. Temperature Dependence (CDCl_3) and Solvent Dependence (24°) of ^1H Chemical Shifts of **2**^{a)}

Temp. [$^\circ\text{C}$]/Solvent	H–C(1)/H–C(8)	H–C(2)/H–C(7)	H–C(3)/H–C(6)	H–C(4)/H–C(5)
+ 50 $^\circ$	7.21	6.89	7.00	7.04
+ 40 $^\circ$	7.23	6.91	7.12	7.07
+ 30 $^\circ$	7.25	6.94	7.15	7.09
+ 20 $^\circ$	7.26	6.97	7.15	7.11
+ 10 $^\circ$	7.28	6.99	7.17	7.13
0 $^\circ$	7.32	7.05	7.21	7.18
– 10 $^\circ$	7.34	7.08	7.24	7.21
– 20 $^\circ$	7.34	7.08	7.24	7.21
– 30 $^\circ$	7.37	7.12	7.28	7.24
– 40 $^\circ$	7.41	7.17	7.23	7.28
– 50 $^\circ$	7.47	7.22	7.37	7.34
$\Delta\delta_{\text{max}}$ [ppm]	0.26	0.33	0.37	0.30
CDCl_3	7.26	6.97	7.15	7.11
(D_6) Benzene	7.63	7.44	$\sim 7.61^{\text{b)}$	$\sim 7.58^{\text{b)}$
(D_6) Acetone	7.36	6.97	7.08	7.03
CD_3CN	7.38	6.97	$\sim 7.01^{\text{b)}$	$\sim 7.01^{\text{b)}$
$\Delta\delta_{\text{max}}$ [ppm] ^{c)}	0.12	0.00	– 0.14	– 0.10

^{a)} Shifts determined by approximate analysis, not by simulation/iteration. ^{b)} Overlap of signals results in approximate δ values. ^{c)} Maximum deviation of δ values in polar solvents from CDCl_3 . Solvent effects observed in benzene are of different origin and not included.

Table 6. Temperature (CDCl₃) and Solvent Dependence (24°) of ¹³C Chemical Shifts of **2**

Temp. [°C]/Solvent	C(1)/C(8)	C(2)/C(7)	C(3)/C(6)	C(4)/C(5)
+ 20°	113.9	107.5	113.6	112.6
+ 10°	113.5	107.4	113.4	112.5
0°	113.5	107.4	113.2	112.4
– 10°	113.4	107.4	113.1	112.3
– 20°	113.3	107.3	112.9	112.2
– 30°	113.1	107.3	112.8	112.0
– 40°	113.0	107.2	112.6	111.9
– 50°	112.8	107.2	112.4	111.8
$\Delta\delta_{\max}$ [ppm]	1.1	0.3	1.2	0.8
CDCl ₃	113.9	107.5	113.6	112.6
(D ₈) THF	114.7	108.8	114.5	113.5
CD ₂ Cl ₂	113.7	108.2	113.4	112.6
CD ₃ CN	114.1	108.8	113.8	113.1
$\Delta\delta_{\max}$ [ppm] ^{a)}	0.8	1.3	0.9	0.9

^{a)} Maximum shift difference relative to δ -value in CDCl₃.

3. Structure of 11,14-Dithianonapentafulvalene (3). – According to the results presented in *Tables 1–4*, all the ¹H chemical shifts of **3** are in the olefinic range and very similar to that of nonafulvene **1f** which belongs to the class *A* of typically olefinic nonafulvenes. Similarly, ³*J* values are strongly alternating and very similar to those of averaged ³*J* pairs of **1b** [4]⁹⁾, which is a type-*A* nonafulvene as well. The same conclusion even holds for all long-range coupling constants⁹⁾. Furthermore, ¹³C chemical shifts of **3** and **1f** are nearly identical, while the shifts of **3** are very similar to the averaged shifts of pairs of C-atoms of **1b** as well (with the exception of C(9)). Finally, ¹H as well as ¹³C chemical shifts are not influenced by variation of temperature (*Table 4*) nor by changes of solvents [13]. These results clearly demonstrate that 11,14-dithianonapentafulvalene (**3**) is a typically olefinic nonafulvene with a non-planar nine-membered ring.

4. Structure of 11,12-Bis(diethylamino)nonatriafulvalene (2). – At room temperature, all NMR parameters of CDCl₃ solutions of **2** are very different from those of type-*A* nonafulvenes **1b** or **1e** as well as of fulvalene **3** (see *Tables 1–6*).

Compared with **1b**, **1e**, and **3**, all the ring protons of **2** undergo an average high-frequency (low-field) shift of 1.3 ppm and absorb in the range between 7.0 and 7.3 ppm (*Table 1*). Similarly to the dipolar form **1c**[±] [11] (being existent at –80° [8]), this is best explained with a planarization of the nine-membered ring: due to the 10 π system of the cyclononatetraenide unit of **2**[±], the ring protons are shifted to the ‘aromatic range’¹⁰⁾.

⁹⁾ All coupling constants of nonafulvalene **3** are nearly identical to those of nonafulvene **1f** [12] as well. The reason why *J* values of **1b** have been entered into *Table 2* is a) because, contrary of **1f**, the ¹H-NMR spectrum of **1b** has been fully analyzed so that *J* values are very exact, and b) because **1b** is an unsymmetrically substituted nonafulvene showing different couplings for diastereotopic ring segments.

¹⁰⁾ This ‘ring-current effect’ is obviously insufficiently counterbalanced by the charge-density effect of the negative charge being distributed over nine C-atoms. Contrary, going from cyclopentadiene to cyclopentadienide, chemical shifts of vinylic ring protons remain nearly constant.

Furthermore, according to *Table 2*, 3J values over formal single bonds of **2** are very large and of the same size as 3J couplings over formal double bonds. This is exactly the effect which is expected for a planarization of the nine-membered ring combined with a complete (or nearly complete) π delocalization resulting in similar bond-lengths of all ring C,C bonds of **2[±]**. Additionally, contrary to **1b**, **1e**, and **3**, all long-range couplings of **2** are very small, because, for planar systems, π contributions to 3J , 4J , and 5J couplings¹¹⁾ are approaching zero.

A dramatic change is observed in the ^{13}C -NMR spectra as well (*Table 3*): proton-bearing ring C-atoms C(1)–C(8) of **1b**, **1e**, **1f**, and **3** absorb between 130 and 121 ppm (*Table 3*) and nearly do not change from compound to compound, while C(9) (which is sensitive to substituents) absorbs between 108 and 122 ppm. However, for nonatriafulvalene **2**, all these C-atoms are strongly shifted to lower frequencies and absorb between 107.4 and 113.5 ppm (C(1)–C(8)) and at 97.8 ppm (C(9)). Going from olefinic nonafulvenes **1b**, **1e**, **1f**, **3** to nonatriafulvalene **2**, there is a very pronounced low-frequency (high-field) shift of -15.9 ppm per C-atom! In the light of the conclusion based on ^1H -NMR data (see above) supporting a highly planarized and delocalized nine-membered ring, the observed low-frequency shift of ring C-atoms of **2** is very reasonably explained by the increased negative π -charge density¹²⁾ according to **2[±]**! It is interesting to test the validity of this explanation based on the fact that a low-frequency shift of 160 ppm per negative charge is expected for olefinic and aromatic molecules of similar steric environment [15]¹³⁾. Based on formula **2[±]**, the negative charge will be fully delocalized over nine C-atoms. Therefore, one would expect a low-frequency shift of $160/9 = 17.8$ ppm per C-atom of **2[±]** which is close to the observed $\Delta\delta$ ¹³⁾.

The most important NMR parameters of 11,12-bis(diethylamino)nonatriafulvalene (**2**) as well as of olefinic nonafulvenes are summarized in *Table 7*. The change from typically olefinic nonafulvenes and nonafulvalenes of type **1b**, **1e**, **1f**, and **3** to nonatriafulvalene **2** is NMR-spectroscopically characterized by a shift of ring protons from the olefinic to the aromatic range, by a dramatic increase of 3J couplings over formal single bonds (and a slight increase of 3J couplings over formal double bonds¹⁴⁾) and by a low-frequency shift of nine-membered-ring C-atoms. All these changes are perfectly compatible with dipolar form **2[±]** being characterized by a planarized cyclononatetraenide ring.

If all the NMR results point at dipolar structure **2[±]**, the cyclopropenylum structure of the three-membered ring of **2[±]** should be reflected in the spectroscopic data as well. *Table 8* conclusively shows that the NMR data of the '2,3-bis(diethylamino)cyclopropen-

¹¹⁾ According to stereomodels (and in agreement with the NMR results, see *Table 2*, last two lines), $J(2,5)$ and $J(4,7)$ are expected to be large for non-planar nonafulvenes due to the overlap of the appropriate C–H orbitals (e.g. C(2)–H and C(5)–H) with the p orbitals of the intermediate C=C bond (e.g. C(3)=C(4)).

¹²⁾ Since the early days of ^{13}C -NMR spectroscopy, it is well-known that an increase of π -charge density induces a low-frequency shift of olefinic and aromatic C-atoms [16]. If steric effects are small, then ^{13}C chemical shifts of well-defined systems may be linearly correlated with π -charge density. From the slopes of such correlations, a low-frequency shift of 160 ppm/electron may be derived [15].

¹³⁾ Considering the fact that all the reference compounds **1b**, **1e**, **1f**, **3** are already weakly polarized, one would expect that the observed $\Delta\delta$ should be somewhat smaller than 17.8 ppm.

¹⁴⁾ This is at first sight surprising, because π delocalization induces an increase of bond lengths of formal double bonds which should reduce $J(1,2) = J(7,8)$ and $J(3,4) = J(5,6)$. However, one has to keep in mind that planarization changes the geometry of the nine-membered ring. So, all the H–C–C angles are considerably decreasing which is expected to increase 3J values.

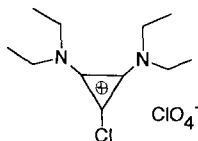
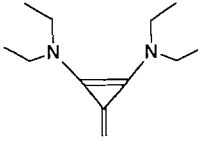
Table 7. Changes of NMR Parameters from **1b**, **1e**, **1f**, and **3** (averaged) to Nonatriafulvalene **2**

	1b , 1e , 1f , 3 ^{a)}	2	$\Delta\delta$ [ppm]
$\delta(\text{H}-\text{C}(1)/\text{H}-\text{C}(8))$	5.96	7.29	1.33
$\delta(\text{H}-\text{C}(2)/\text{H}-\text{C}(7))$	5.54	7.00	1.46
$\delta(\text{H}-\text{C}(3)/\text{H}-\text{C}(6))$	6.02	7.17	1.15
$\delta(\text{H}-\text{C}(4)/\text{H}-\text{C}(5))$	5.80	7.12	1.32
			$\overline{\Delta\delta} = 1.32 \text{ ppm}$
$J(1,2)/J(7,8)$	12.4	13.6	1.2
$J(2,3)/J(6,7)$	3.9	11.8	7.9
$J(3,4)/J(5,6)$	12.1	13.2	1.1
$J(4,5)$	2.9	11.7	8.8
			$\overline{\Delta J} = 4.75 \text{ Hz}$
$\delta(\text{C}(1)/\text{C}(8))$	128.7	113.5	-15.2 ppm
$\delta(\text{C}(2)/\text{C}(7))$	123.8	107.4	-16.4
$\delta(\text{C}(3)/\text{C}(6))$	128.4	113.2	-15.2
$\delta(\text{C}(4)/\text{C}(5))$	126.4	112.4	-14.0
$\delta(\text{C}(9))$	116.6	97.8	-18.8
			$\overline{\Delta\delta} = -15.9 \text{ ppm}$

^{a)} Averaged δ and 3J values over all four compounds.

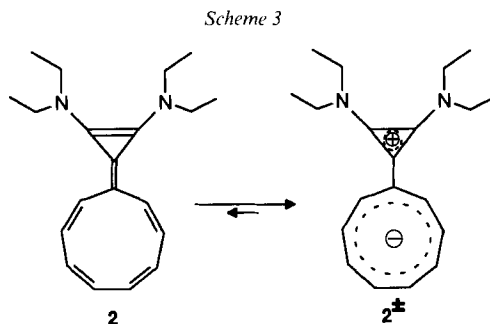
1-ylidene unit' of **2** are in fact very similar to those of 1-chloro-2,3-bis(diethylamino)-cyclopropenylium perchlorate (**4**) which points at a positively charged cyclopropenylium unit of **2**: both in the ^1H -NMR as well as in the ^{13}C -NMR, the signals of the $\text{N}-\text{CH}_2$ group are at very high frequency, and the vinylic C-atoms bearing N are comparable (133.4 and 128.9 ppm, respectively). Furthermore, rotation around C-N bonds is blocked at low temperature, although less hindered for **2** where, at 400 MHz and in CDCl_3 , coalescence is observed around -25° ($\text{N}-\text{CH}_2$ groups) so that at room temperature only one set of $\text{N}-\text{CH}_2-\text{CH}_3$ signals is visible both in the ^1H - and in the ^{13}C -NMR.

Table 8. ^1H - and ^{13}C -NMR Data of the Cyclopropenylium Units of Perchlorate **4** and Nonatriafulvalene **2**

				
	4	4	2	2
^1H -NMR (CDCl_3) ^{a)}	3.52(<i>q</i>)	3.49(<i>q</i>)	3.85(<i>q</i>)	3.46(<i>q</i>)
	1.33(<i>t</i>)	1.29(<i>t</i>)	1.42(<i>t</i>)	1.36(<i>t</i>)
^{13}C -NMR (CDCl_3) ^{a)}	133.4(<i>s</i>)	92.5(<i>s</i>) ^{b)}	128.9(<i>s</i>)	127.8(<i>s</i>) ^{b)}
	48.8(<i>t</i>)	47.2(<i>t</i>)		47.4(<i>t</i>)
	13.7(<i>q</i>)	13.5(<i>q</i>)		14.7(<i>q</i>)

^{a)} Rotation around exocyclic C-N bonds is more hindered in **4** than in **2**: ^1H - and ^{13}C -NMR spectra of **2** show at r.t. only signals of one $\text{N}-\text{CH}_2\text{CH}_3$ group. Coalescence temperature for $\text{N}-\text{CH}_2$ quartets (400 MHz, CDCl_3): -25° . ^{b)} Due to marked structural differences, Cl-bearing C-atom of **4** is not comparable to C(10) of fulvalene **2**!

All these results demonstrate that CDCl_3 solutions of nonatriafulvalene **2** display at room temperature all the features of dipolar cyclopropenylium-cyclononatetraenide 2^\pm (Scheme 3).



Considering an equilibrium $2 \rightleftharpoons 2^\pm$ (being completely on the side of dipolar 2^\pm even in unpolar solvents like CDCl_3 and at room temperature) and remembering the fact that the well-established equilibrium $1c \rightleftharpoons 1c^\pm$ induces temperature and solvent-dependent shifts of NMR signals, we investigated the behavior of **2** in a broad temperature and solvent range (Tables 5 and 6).

If the temperature of CDCl_3 solutions of **2** is changed from $+50$ to -50° , a slight average shift (0.32 ppm) of all ring protons to higher frequencies is observed. This would be a small shift in the right direction¹⁵, because dipolar 2^\pm is expected to be favored at low temperature. On the other hand, changing solvent polarity from CDCl_3 to (D_6)acetone or CD_3CN , which should strongly favor 2^\pm as well, does not affect ^1H chemical shifts (Table 5) at all¹⁵, while the changes observed in unpolar (D_6)benzene have to be attributed to the considerable anisotropy of the solvent.

To look at the inconsistency¹⁵ of solvent and temperature effects on ^1H chemical shifts, we checked changes of ^{13}C chemical shifts as well. Table 6 conclusively demonstrates that ^{13}C chemical shifts are virtually not influenced by temperature or solvents. We, therefore, assume that the slight high-frequency shifts of the ^1H -NMR signals between $+50^\circ$ and -50° are not the result of a marked change of the equilibrium $2 \rightleftharpoons 2^\pm$ ¹⁶.

5. Discussion. – Our investigations show that all the NMR parameters of 11,12-bis-(diethylamino)nonatriafulvalene (**2**) are dramatically different from those of all known type-*A* and type-*B* nonafulvenes. They are similar to the results obtained for 10,10-bis-(dimethylamino)nonafulvene [8] at low temperature ([6] [7] [12]) and consistent with Boche's hypothesis proposing the existence of dipolar $1c^\pm$ at low temperature [11]. Contrary to $1c \rightleftharpoons 1c^\pm$, however, the NMR parameters of **2** are not significantly influenced by changes of temperature or solvent polarity.

¹⁵ Taking the $\Delta\delta$ values of Table 7 as a standard, lowering temperature by 100° (Table 5, above) seems to influence ^1H chemical shifts by 24%, but solvent effects (Table 5, below) make only 2%! On the other hand, both temperature and solvent effects (Table 6) on ^{13}C chemical shifts are very small (5% and 6% relative to the standard of Table 7).

¹⁶ So far, the reason for the slight temperature effect on ^1H -chemical shifts is unknown. It is easily possible that solvation of 2^\pm (and especially the number of solvated CDCl_3 molecules) changes with temperature.

The obvious conclusion is that the correct structure describing the spectroscopic behavior¹⁷⁾ of **2** is that of a cyclopropenylium cyclononatetraenide 2^\pm . This means that, according to the classification of nonafulvenes given in the introduction, **2** is the first nonafulvene of the so far unknown class D!

Therefore, if exocyclic substituents of the nonafulvene unit are systematically changed, NMR parameters should be dependent on the relative energies of the olefinic form **1** and of the dipolar planarized form 1^\pm , **1a**, and **2** being the extremes. As long as the olefinic form **1** is predominant, substituent effects are expected to influence NMR parameters of ring protons and ring C-atoms only moderately, so that the NMR data of all nonafulvenes of type A or type B are in a relatively narrow range. However, if $1c \rightleftharpoons 1c^\pm$ really links the extremes **1a** and **2**, then the temperature-dependent plot of NMR data of $1c \rightleftharpoons 1c^\pm$ should link the data of 'unpolar nonafulvenes' of type A and type B with those of dipolar 2^\pm .

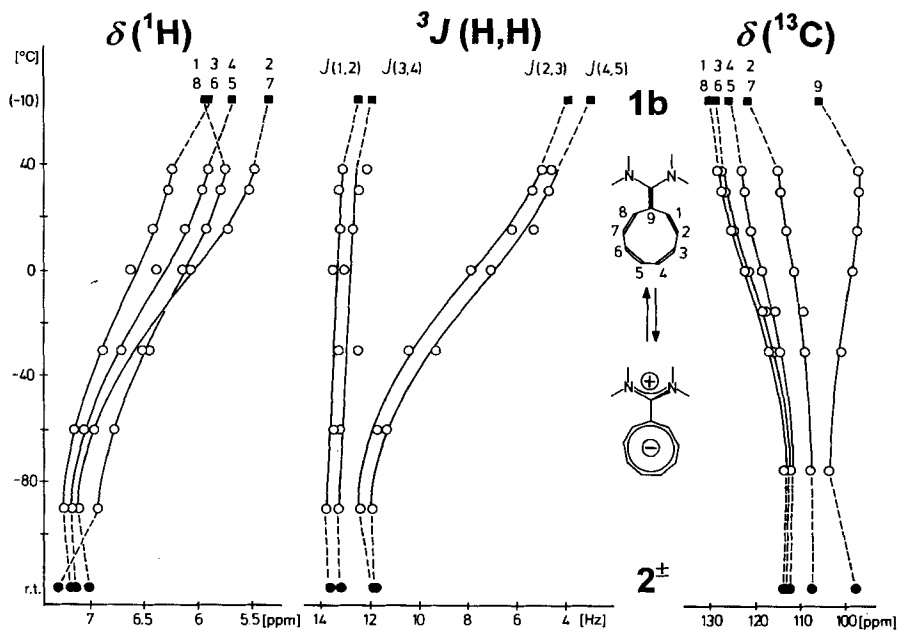


Fig. 4. NMR Parameters of 10-(dimethylamino)nonafulvene (**1b**; top, (D₆)acetone, -10°) as a type-A nonafulvene, of 10,10-bis(dimethylamino)nonafulvene (**1c**; CD₂Cl₂, range between +38° and -90°) as a type-C nonafulvene, and of 11,12-bis(diethylamino)nonatriafulvalene (**2**; bottom, CDCl₃, r.t.) as a type-D nonafulvene¹⁸⁾ ¹⁹⁾

¹⁷⁾ It is interesting to note that the UV absorption of CHCl₃ solutions of **2** ($\lambda_{\max}(\epsilon)$: 255 (8590, sh), 290 (12900), 407 (8650)) are very similar to those of CH₂Cl₂ solutions of **4c** at -80° (λ_{\max} : 240, 290, 410 [9] [10]) and strongly different from those of CHCl₃ solutions of **4c** at r.t. (λ_{\max} : 340).

¹⁸⁾ Due to the different substitution pattern of nonafulvenes **1b**, **1c**, and nonafulvalene **2**, chemical shifts of C(10) (not given here) and of C(9) cannot be compared. Small but systematic deviations of all the NMR parameters of **1b** and **1c** (at 38°) support the conclusion that at 38° the equilibrium $1c \rightleftharpoons 1c^\pm$ is not yet completely on the side of olefinic **1c** (see Fig. 4).

¹⁹⁾ Fig. 4 contains averaged δ values of pairs of ring protons (Table 1), and ring C-atoms (Table 3), and averaged pairs of $^3J(\text{H,H})$ coupling constants (Table 2) of **1b**.

As *Fig. 4* shows, this is in fact the case. Taking into account that C(9) of **1b**, **1c**, and **2** cannot be compared due to the different steric effects, and that electronic substituent effects influence $C(9) > C(2,7) > C(4,5)$, the agreement is outstanding: ^1H chemical shifts, $^3J(\text{H,H})$ values, and ^{13}C chemical shifts of nonplanar olefinic nonafulvenes like **1b** are related to the ‘high-temperature form’ **1c**¹⁸, while all the NMR parameters of **2** are nearly identical with the ‘low-temperature form’ **1c**[±].

The work presented here shows that dipolar nonafulvenes with a planarized nine-membered ring (see **2**[±]) are existing in the usual temperature range and even up to 50° and in unipolar solvents. Their spectroscopic properties dramatically differ from those of non-planar olefinic nonafulvenes like **1a**, **1b**, and **1e** (or of nonafulvenes like **3**). These two types of nonafulvenes are interconnected by nonafulvenes like **1c** whose olefinic form **1c** and dipolar form **1c**[±] are very similar in energy so that either **1c** or **1c**[±] may be predominant depending on the experimental conditions [11]. So, the whole range of nonafulvenes has been made available, starting with the parent compound **1a** ($R^1 = R^2 = \text{H}$ [3]) on one side, and ending with substituted cyclopropenylium cyclo-nonatetraenide **2**[±] [1] on the other side. *Hafner*'s nonafulvene **1c** [8] is not a spectacular exception, but systematically links type-*A* (**1a**, **1b**) and type-*B* nonafulvenes (**1d**) (see *Fig. 2*) with type-*D* nonafulvenes like **2**.

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Experimental Part

Syntheses. – Nonafulvenes **1b** [17], **1c** [9] [18], **1e** [1] [13], **1f** [18] as well as nonafulvalenes **2** [1] [13], and **3** [1] [13] have been prepared according to literature procedures.

NMR Spectra. – *General.* ^1H -NMR Spectra of carefully filtered and degassed solns. of **1b**, **1c**, **1e**, **1f**, and of nonafulvalenes **2** and **3** were recorded in solvents and at temperatures given in *Tables 1*, *2*, and *5* with a *Bruker AM-400* spectrometer. Typical parameters to achieve high-resolution spectra, being necessary for a successful spin analysis, were: spectral width 4800 Hz, 64-K data points, corresponding to a digital resolution of 0.15 Hz/Pt, acquisition time 6.82 s, pulse width 13 μs , relaxation delay 6.0 s. For resolution enhancement, a *Gaussian* function was used with a line broadening of -0.2 Hz and a *Gaussian* constant of 0.15. The FID was zero-filled to 32 K prior to *Fourier* transformation. Simulations and iterations were performed on a *Bruker* computer of the type *Aspect 2000* with 256 K of memory, multicolor graphics display, floppy disc *FDD 280* and an analogue recorder. For simulations and iterations, the program PANIC was used [19].

Additionally, the high-resolution ^1H -NMR spectrum of nonafulvalene **2** was recorded on a *Bruker AMX-600* spectrometer in CDCl_3 at r.t., with the following acquisition parameters: spectral width 4545 Hz, 128-K data points, corresponding to a digital resolution of 0.07 Hz/Pt, pulse width 5 μs , relaxation delay 1 s, acquisition time 14.42 s. Resolution enhancement and zero filling was applied as well (see above).

^{13}C -NMR Spectra have been recorded in solvents and at temp. given in *Tables 3*, *4* and *6*. Assignments were based on prior assignment of ^1H -NMR spectra followed by recording ^{13}C , ^1H -correlated 2D spectra [20].

^1H -NMR Analysis of 11,14-Dithianonapentafulvalene (**3**). Chemical shifts and splitting pattern of CD_2Cl_2 solns. of **3** are very similar to those of 10,10-(ethylenedithio)nonafulvene (**1f**) (*Tables 1* and *2*) which has been analyzed earlier [12] [14]. Therefore, a first simulation was performed with approximate chemical shifts of **3** (taken out of the exper. spectrum) and coupling constants of **1f** [12]. Further improvement was achieved by adding small 4J and 5J couplings $^4J(1,8)$, $^5J(1,4) = ^5J(5,8)$, $^5J(1,7)$, and $^5J(3,6)$ as well as $^6J(1,6)$: the resulting simulated spectrum already strongly resembled the experimental spectrum. Then, 52% of the exper. lines were assigned to theoretical transitions to give, after iteration and final simulation, the spectrum of *Fig. 2* (upper trace). Despite of an *RMS* of 0.73, the calculated as well as the exper. spectrum (*Fig. 2*, lower trace) show a relatively good fit.

¹H-NMR Analysis of 11,12-Bis(diethylamino)nonatriafulvene (**2**). Since ¹H-chemical shifts and splitting patterns of the ¹H-NMR multiplets of **2** are completely different (see Tables 1, 2), unpolar nonafulvenes of classes A and B are not suited as reference compounds. Furthermore, H–C(3,6) and H–C(4,5) are strongly overlapping at 400 MHz, but separated from H–C(1,8) and H–C(2,7). Additionally, lines of NMR multiplets of **2** are considerably broader than those of **3**, so that the number of lines of **2** is much smaller than that of **3** (see Fig. 3 and 2). Changes of solvents (from CDCl₃ of Fig. 3 to CD₂Cl₂, (D₆)acetone, CCl₄/CDCl₃, (D₆)benzene, (D₈)THF) or applying shift reagents did not improve separation of proton signals nor resolution (or the number of lines).

In a first attempt, roughly approximate ³J coupling constants were extracted from the 400-MHz multiplets of H–C(1,8) and H–C(2,7) which indicated that ³J coupling constants $J(1,2) = J(7,8)$ and $J(2,3) = J(6,7)$ must be of the same size. Together with the fact that δ values of **2** are in the 'aromatic range', this was a strong clue for **2** existing in the dipolar form **2**[±]. This prompted us to simulate the spectrum of **2** with the ³J coupling constants obtained for 10,10-bis(dimethylamino)nonafulvene (**1c**) in CD₂Cl₂ at –90° [12] [14]²⁰⁾. Considering the very approximate procedure, neglecting all the long-range couplings, the similarities between the experimental as well as the simulated spectrum (Fig. 5) are quite surprising.

To improve separation of overlapping multiplets of H–C(3)/H–C(6) and H–C(4)/H–C(5), a 600 MHz ¹H-NMR spectrum was recorded (CDCl₃, r.t.), and a first simulation was performed with δ and ³J values obtained at 400 MHz (Fig. 5). Subsequently, an iteration was made (based on the simulated spectrum) by varying all the δ and ³J values, but still neglecting all the long-range couplings. The resulting set of δ and ³J values²¹⁾ gave, after simulation, the spectrum given in Fig. 6 (second trace from below). If one takes into account that all ⁴J and ⁵J

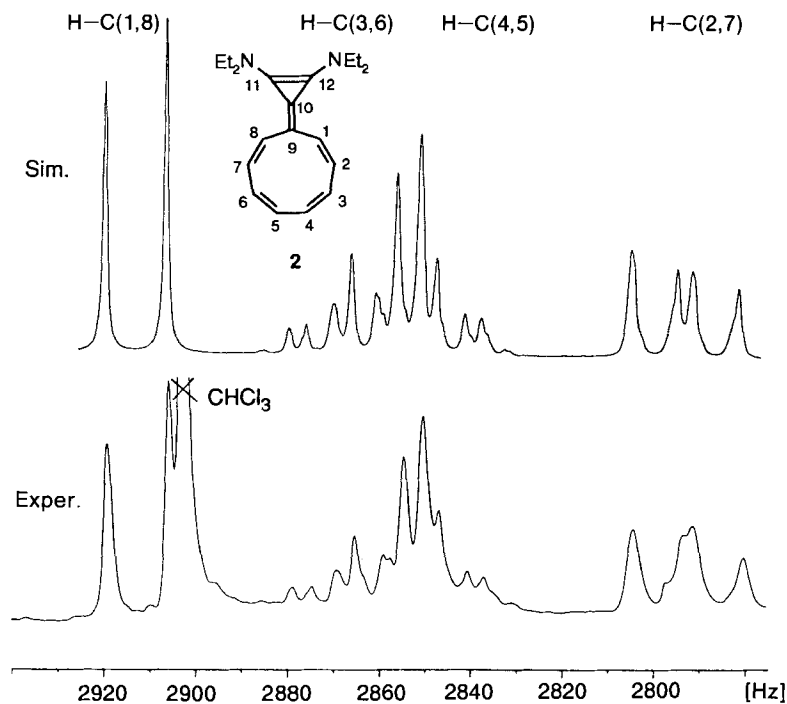


Fig. 5. Result of a first rough approximation of the ¹H-NMR spectrum of **2** (lower trace, 400 MHz, CDCl₃, r.t.) by simulation with approximate δ values of **2** and ³J values of **1c** (400 MHz, CD₂Cl₂, –90°) [12] [14]

²⁰⁾ For **1c**, an equilibrium $1c \rightleftharpoons 1c^{\pm}$ has been established (see Introduction). At –90° and in polar solvents, the equilibrium is strongly in favor of **1c**[±]: in CD₂Cl₂ at –90°, ³J values over formal single bonds of **1c** ($J(2,3) = J(6,7) = 12.4$ and $J(4,5) = 11.9$ Hz) are close to those over formal double bonds of **1c** ($J(1,2) = J(7,8) = 13.8$ and $J(3,4) = J(5,6) = 13.3$ Hz) [12].

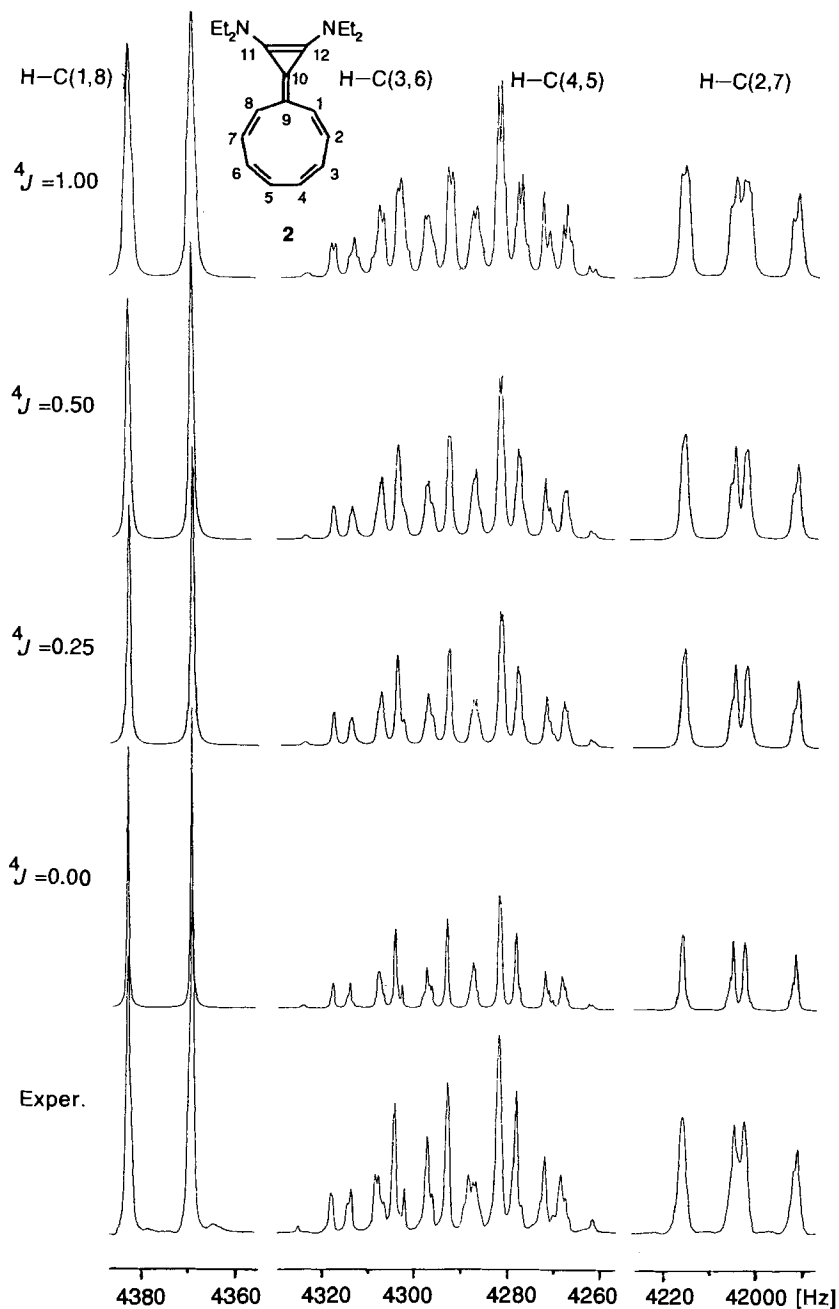


Fig. 6. 600-MHz $^1\text{H-NMR}$ Spectrum (CDCl_3 , r.t.) in the range between 6.9 and 7.35 ppm (lowest trace); series of simulations²¹⁾ with 4J values between 0.0 and 1.0 Hz

²¹⁾ δ : $\text{H-C}(1,8)$: 7.29; $\text{H-C}(2,7)$: 7.01; $\text{H-C}(3,6)$: 7.17; $\text{H-C}(4,5)$: 7.13 ppm. 3J : $J(1,2) = J(7,8) = 13.43$; $J(2,3) = J(6,7) = 11.00$; $J(3,4) = J(5,6) = 13.20$; $J(4,5) = 10.50$ Hz.

couplings have been arbitrarily set zero, the fit with the experimental spectrum (Fig. 6, lowest trace) is surprising; it is only possible if the long-range couplings are small. Therefore, line forms and line-widths were approximated by simultaneously increasing all the 4J values in small steps. According to simulations given in Fig. 6, the best fit results with 4J values between 0 and 0.25 Hz.

Finally, the last iteration was performed with an initial setting of all $^4J = 0.25$ Hz by varying all the parameters (including δ , 3J , and 4J) values to give the final simulation of Fig. 3 and the parameters of **2** given in Tables 1 and 2.

NMR Parameters of 1c. Additionally to the values published in [12], ^1H and ^{13}C chemical shifts and especially $^3J(\text{H,H})$ values of **1c** have been determined in the temperature range from 0° to 38° on a Bruker AC-300 spectrometer in CD_2Cl_2 (plots see Fig. 4):

$\delta(^1\text{H})$ [ppm]: H–C(1)/H–C(8): 6.141 (0°); 5.910 (15°); 5.780 (30°); 5.748 (38°). H–C(2)/H–C(7): 6.071 (0°); 5.717 (15°); 5.519 (30°); 5.466 (38°). H–C(3)/H–C(6): 6.623 (0°); 6.409 (15°); 6.270 (30°); 6.231 (38°). H–C(4)/H–C(5): 6.385 (0°); 6.112 (15°); 5.945 (30°); 5.899 (38°). NMe_2 : 2.92 (0°); 2.83 (15°); 2.79 (30°); 2.78 (38°).

$\delta(^{13}\text{C})$ [ppm]: C(1)/C(8): 121.70 (0°); 124.76 (15°); 126.69 (30°); 127.37 (38°). C(2)/C(7): 111.07 (0°); 112.72 (15°); 114.01 (30°); 114.49 (38°). C(3)/C(6): 121.26 (0°); 124.66 (15°); 126.20 (30°); 126.76 (38°). C(4)/C(5): 118.21 (0°); 120.43 (15°); 121.88 (30°); 122.37 (38°). C(9): 98.21 (0°); 97.01 (15°); 96.75 (30°); 96.81 (38°). C(10): 174.25 (0°); 169.82 (15°); 167.05 (30°); 166.12 (38°).

$^3J(\text{H,H})$ [Hz] after simulation and iteration with PANIC [19]: $J(1,2)/J(7,8)$: 13.55 (0°); 13.24 (15°); 13.30 (30°); 13.17 (38°). $J(2,3)/J(6,7)$: 7.87 (0°); 6.20 (15°); 5.38 (30°); 4.99 (38°). $J(3,4)/J(5,6)$: 13.12 (0°); 12.77 (15°); 12.51 (30°); 12.16 (38°). $J(4,5)$: 7.05 (0°); 5.31 (15°); 4.75 (30°); 4.74 (38°).

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