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# The $^{19}F$ NMR spectra of fluorinated cyclohexadienes and prediction of the chemical shifts in fluorinated 1,4-cyclohexadienes, 1,4-cyclohexadien-3-ones, cyclohexenes and cyclohexen-3-ones

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**Abstract**

A compilation of the $^{19}F$ NMR spectral data of fluorinated cyclohexadienes is presented. The effects of common substituents were determined and used for the prediction of the $\delta$ (F) values of fluorinated 1,4-cyclohexadienes, 1,4-cyclohexadien-3-ones, cyclohexenes and cyclohexen-3-ones. 

*Keywords:* Fluorinated cyclohexadienes; $^{19}F$ NMR spectroscopy; Chemical shifts

## 1. Introduction

$^{19}F$ NMR spectroscopy is a routine method of chemical analysis and there are many handbooks and reviews concerning spectral-structure correlations on polyfluorinated alkanes, alkenes and arenes (see Ref. [1] and references there). However, experimental data on the $^{19}F$ NMR spectra of fluorine-containing cyclohexadienes have not been systematized. Sometimes the original publications differ from each other in values of chemical shifts, coupling constants, by the different interpretations of spectra of the same compound or contain only the list of chemical shifts without assignment. This paper presents the compilation of the reported $^{19}F$ NMR spectra of some fluorinated cyclohexadiene derivatives. On the base of this collection the increments of the common substituents were determined and their applicability for the prediction of the $\delta$ (F) values for fluorinated 1,4-cyclohexadienes, 1,4-cyclohexadien-3-ones, cyclohexenes and cyclohexen-3-ones was demonstrated.

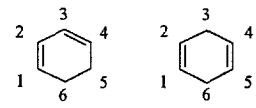
## 2. Results

### 2.1. The $^{19}F$ NMR spectra of fluorinated cyclohexadienes

Tables 1 and 2 contain the chemical shifts $\delta$ (F) and coupling constants in the $^{19}F$ NMR spectra of fluorinated 1,3-cyclohexadienes and values for fluorinated 1,4-cyclohexadienes are given in Tables 3–7.

The published $^{19}F$ NMR spectra were re-calculated using the following standard chemical shifts of the references $\delta$ (F) ($C_6F_6$) −162.9, $\delta$ (F) ($CF_3COOH$) −76.5 and $\delta$ (F) ($C_6H_5CF_3$) −62.0 ppm with respect to $\delta$ (F) ($CFCl_3$) 0.00 ppm.

The positions of substituents in cyclohexadienes are numbered as follows:




For uniformity, this nomenclature is also used for cyclic unsaturated ketones, for example: 1-chloropentafluoro-1,4-cyclohexadien-3-one.

### 2.2. Calculation of the chemical shifts δ (F) in 1,4-cyclohexadiene derivatives

Calculations of chemical shifts on substituent increments are a useful tool for spectral-structure correlations and this method is often used in the NMR spectroscopy [1]. The present collection contains sufficient data for incremental analysis of the $\delta$ (F) values of fluorinated 1,4-cyclohexadienes. The spectra of their conjugated isomers are often not interpreted and their number is insufficient for such analysis.

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Table 1
Chemical shifts (in ppm) of fluorine-containing 1,3-cyclohexadienes

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| F | | −151.7 | −160.8 | −160.8 | −151.7 | −124.2 | −124.2 | [2] |
| | $CDCl_3$ | −151.6 | −161.4 | −161.4 | −151.6 | −124.2 | −124.2 | [3] |
| 1-H | $CDCl_3$ | n.d. (H) | −134.6 | −156.2 | −151.5 | −125.7 | −120.5 | [3] |
| 1-$CH_3$ | | 1.55 (H) | [−130.3, | −150.0, | −160.7*] | −124.3 | −118.9 | [4] |
| 1-$CF_3$ | | −58.4 | −110.0 | *−152.1* | *−150.4* | *−125.9* | *−118.2* | [5][c] |
| 1-$C_6F_5$ | $CCl_4$ | [a] | −111.51 | −152.9 | −150.9 | −126.1 | −117.6 | [6] |
| | $CDCl_3$ | | −113.1 | −152.5 | −150.6 | −127.0 | −117.8 | V.V. Bardin, unpublished results |
| 1-$OCH_3$ | | 3.45 (H) | −154.8* | −158.0 | −162.6* | −135.9 | −120.9 | [4] |
| 1-$SiF_3$ | $SO_2FCl$ | −134.9 | −93.5 | −146.5 | −150.3 | −126.0 | −111.4 | [7] |
| 2-$CH_3$ | | * | 1.63 (H) | [−138.0, −154.9, −166.9*] | | −125.1 | −124.3 | [4] |
| 2-$OCH_3$ | | * | 3.80 (H) | [−147.1, −165.3, −169.5*] | | −121.6 | −123.8 | [4] |
| 2-$OC_2H_5$ | $CCl_4$ | * | 1.38 (H) | −167.0, | −168.5, | −122.3, | −124.3* | [8] |
| | | | 4.31 (H) | −147.0* | | | | |
| 5-$OCF_3$ | | −151.3 | −155.3 | −155.3 | −147.0 | −122.2 | ≈ −113 | [9] |
| | | | | | | −57.4 ($OCF_3$) | | |
| 5,6-$Cl_2$ (*Z*) | $CDCl_3$ | −149.6 | −154.0 | −154.0 | −149.6 | −129.0 | −129.0 | [10] |
| 5,6-$Cl_2$ (*E*) | $CDCl_3$ | −151.0 | −154.6 | −154.6 | −151.0 | −120.8 | −120.8 | [10] |
| 5,6-O[b] | $CH_2Cl_2$ | −149.2 | −152.8 | −152.8 | −149.2 | −154.3 | −154.3 | [11] |
| 5-$CH_2OH$ | | *−139.5* | *−154.9* | *−154.9* | *−139.5* | *−167.3* | *−169.9* | [12] |
| 6-H | | | | | | | | |
| 5-R[c] | $CCl_4$ | −146.3 or | −152.3 or | −153.8 or | −146.9 or | −164.3 | −170.3 | [13] |
| 6-H | | −146.9 | −153.8 | −152.3 | −146.3 | | 4.63 (H) | |
| 1,2-$H_2$ | $CDCl_3$ | n.d. (H) | n.d. (H) | −109.8 | −135.5 | −126.9 | −119.0 | [3] |
| 1,2-$(CH_3)_2$ | $CCl_4$ | 1.89 (H) | 1.89 (H) | [−141.7, | −160.1*] | −123.6, | −128.4* | [14] |
| 1-$OCH_3$, | | 3.5 (H) | 6.1 (H) | n.d. (H) | n.d. (H) | n.d. (H) | n.d. (H) | [15] |
| 2-H | | | | | | | | |
| 1-H | $CCl_4$ | 6.70 (H) | −121.7 or | −147.8 or | −156.7 or | −127.5 | −120.1 | [16] |
| 2-$CHF_2$ | | | −120.6 | −137.3 | −157.7 | | | |
| and | | | 6.40 (H) | | | | | |
| 1-$CHF_2$ | | −120.6 or | 6.30 (H) | | | | | |
| 2-H (mixture) | | −121.7 | | | | | | |
| 1,3-$H_2$ | $CDCl_3$ | n.d. (H) | −124.9 | n.d. (H) | −101.8 | −130.8 | −114.9 | [17,3] |
| 1,3-$(C_6F_5)_2$ | $CCl_4$ | [d] | −100.3 | [d] | −113.7 | −130.5 | −119.0 | [18] |
| 1,4-$H_2$ | | 5.77 (H) | −121.8 | −121.8 | 5.77 (H) | −116.0 | −116.0 | [19] |
| | $CDCl_3$ | n.d. (H) | −121.6 | −121.6 | n.d. (H) | −116.0 | −116.0 | [3] |
| 1,4-$(CF_3)_2$ | | −59.0 | −120.0 | −120.0 | −59.0 | −111.6 | −111.6 | [20] |
| 1-$CF_3$ | $CH_2Cl_2$ | −58.6 | −110.1 | −120.3 | 6.00 (H) | −119.1 | −115.6 | [21] |
| 4-H | | | | | | | | |
| 1-$CF_3$ | ether | −58.1 | −108.3 | −112.4 | − | −120.2 | −116.2 | V.V. Bardin, unpublished results |
| 4-$NO_2$ | | | | | | | | |
| 2,3-$(CH_3)_2$ | $CCl_4$ | −140.5 | 1.85 (H) | 1.85 (H) | −140.5 | −127.2 | −127.2 | [14] |

(*continued*)

Table 1 (*continued*)

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 2,3-$(CF_3)_2$ | $CCl_4$ | −113.0 | −60.3 | −60.3 | −113.0 | −133.0 | −133.0 | [22] |
| 2-H, 3-$OCH_3$ | | −134.3 | 5.09 (H) | 3.66 (H) | −175.1 | −126.6* | −127.3* | [15] |
| 1,2,3-$H_3$ | $CDCl_3$ | n.d. (H) | n.d. (H) | n.d. (H) | −130.1 | −132.5 | −120.6 | [17] |
| 1,3,4-$H_3$ | $CDCl_3$ | n.d. (H) | −105.7 | n.d. (H) | n.d. (H) | −116.8 | −122.4 | [17] |
| 1,2,3,4-$H_4$ | hexane | n.d. (H) | n.d. (H) | n.d. (H) | n.d. (H) | −122.7 | −122.7 | [23] |
| | $CDCl_3$ | n.d. (H) | n.d. (H) | n.d. (H) | n.d. (H) | −123.1 | −123.1 | [17] |
| 1,2,4-$H_3$ | | n.d. (H) | n.d. (H) | – | n.d. (H) | −118.9 | −123.3 | K. Momota, personal communication |
| 3-Cl | | | | | | | | |
| 2,3,5,6-$(CF_3)_4$ (*Z*) | | −108.0 | −59.5 | −59.5 | −108.0 | −201.4, −75.5 ($CF_3$) | −201.4, −75.5 ($CF_3$) | [24] |
| 1,2,3,4,5-$(CF_3)_5$ | | −57.9 | −70.4 | −70.4 | −70.4 | −159.5, −56.4 ($CF_3$) | −88.0, −52.7 | [25] |
| 1-$CF_3$ 2,3,4,5-$H_4$ | $CDCl_3$ | −65.3 | n.d. (H) | n.d. (H) | n.d. (H) | −208.2 | −113.1, −118.3 | [26] |
| 1-$CF_3$ 2,3,4,6-$H_4$ | $CDCl_3$ | −65.7 | n.d. (H) | n.d. (H) | n.d. (H) | −104.8, −121.5 | −198.7 | [26] |

[a] δ (F) ($C_6F_5$): −136.4 (*ortho*), −160.8 (*meta*), −149.3 (*para*) [6]; −136.8 (*ortho*), −160.7 (*meta*), −148.7 (*para*) (V.V. Bardin, unpublished results).
[b] Epoxide.
[c] R = cyclohexyl; δ (H): 2.72 (1 H), 1.06–1.94 (10 H).
[d] δ (F) ($C_6F_5$): −136.8 (*ortho*), −160.7 (*meta*), −148.7 and −150.0 (*para*).
[e] The assignment of the resonances of 1-$CF_3$-1,3-$C_6F_7$ and 1-$CF_3$-1,4-$C_6F_7$ must be interchanged.
n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
*123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

Table 2
Coupling constants of fluorine-containing 1,3-cyclohexadienes

| Substituent | Solvent | J, Hz | Ref. |
|---|---|---|---|
| F | | (1, 2) 2, (1, 3) 10, (1, 4) 1, (1, 5) 5, (1, 6) 15, (2, 3) 1, (2, 4) 10, (2, 5) 6, (2, 6) 10 | [2] |
| 1-$C_6F_5$ | $CDCl_3$ | (2, 3) 6, (2, 4) 8, (2, 5) ≈4, (3, 5) 4, (3, 6) 4, (4, 5) 16 | V.V. Bardin, unpublished results |
| 1-$SiF_3$ | $SO_2FCl$ | (2, 3) 13.5, (2, 4) 10, (2, 5) ≈4, (2, 6) 16, (3, 5) 18, (3, 6) 4, (4, 5) 16, (FSi, 6) 3 | [7] |
| 5-$OCF_3$ | | (6A, 6B) 300 | [9] |
| 1,2-$H_2$ | $CDCl_3$ | *(5, 3)* = *(5, 4)* 19.9 | [3] |
| 1,3-$H_2$ | $CDCl_3$ | *(5, 4)* 19.8, *(6, 2)* 17.4 | [17,3] |
| 1,4-$H_2$ | | (1, 5) 3.7, (1, 6) 15.1, (2, 6) 3.7 | [19] |
| 1-$CF_3$ 4-H | $CH_2Cl_2$ | (2, 3) 7, (2, 5) 7, (2, 6) 17, (3, 4) 7, (3, 5) 17, (4, 5) 8 | [21] |
| 1-$CF_3$ 4-$NO_2$ | ether | (CF3, 2) 24, ($CF_3$, 6) 7, (2, 3) 4, (2, 6) ≈18, (3, 5) 15, (5, 6) 3.5 | V.V. Bardin, unpublished results |
| 5-$CH_2OH$ 6-H | | (5, 6) 24, (5, $CH_2$) 24, (6F, 6H) 50 | [12] |
| 5-*c*-$C_6H_{11}$ 6-H | $CCl_4$ | (5, 6) 21, (6F, 6H) 60 | [13] |
| 1,2,3-$H_3$ | $CDCl_3$ | *(5, 4)* 19.8 | [17] |
| 1,3,4-$H_3$ | $CDCl_3$ | *(5, 2)* 19.8 | [17] |
| 1-$CF_3$ 2,3,4,5-$H_4$ | $CDCl_3$ | (5F, 5H) 44.7, (6A, 6B) 285 | [26] |
| 1-$CF_3$ 2,3,4,6-$H_4$ | $CDCl_3$ | (5A, 5B) 301, (6F, 6H) 44.7 | [26] |

n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
*– 123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

Because the published spectral data are sometimes substantially different from each other, for the accurate determination of the increments of the $^{19}$F NMR spectra of some basic 1-R-heptafluoro-1,4-cyclohexadienes (R = F, H, Br, $CF_3$ and $C_6F_5$) in $CDCl_3$ or $CDCl_3$–$CFCl_3$ solutions (1–5 M%) spectra were re-measured (spectrometer Bruker WP 200 SY or AC 200 at 188.28 MHz, internal reference $C_6F_6$).

The increments of each substituent R (R ≠ F) are divided into two groups: (a) for the residual vinylic fluorine atoms and (b) for allylic ones (Table 8).

### 2.2.1. Prediction of the NMR line position for vinylic fluorine atoms

The δ ($F_{vin}$) values in the 3,3,6,6-tetrafluoro-1,4-cyclohexadiene series were determined from Eq. (1).

$$\delta(F_{vin}) = -(156.3 + a + b + c) \quad (1)$$

The value −156.3 is the chemical shift of the vinylic fluorines in the $^{19}$F NMR spectrum of octafluoro-1,4-cyclohexadiene. In a series of 3-X-3,6,6-trifluoro-1,4-cyclohexadienes or 6,6-difluoro-1,4-cyclohexadien-3-ones the corresponding chemical shifts were calculated from Eqs. (2) and (3).

$$\delta(F-1 \text{ and } 5) = -(K + a + b + c) \quad (2)$$

$$\delta(F-2 \text{ and } 4) = -(L + a + b + c) \quad (3)$$

where $K$ and $L$ are the chemical shifts of the fluorine resonances F-1, 5 and F-2, 6 in the spectrum of perfluoro-3-X-1,4-cyclohexadiene. For example,

X = FCl $K = 159.7$ $L = 149.7$
X = $FNO_2$ $K = 149.2$ $L = 152.8$
X = FH $K = 159.3$ $L = 142.9$
X = O $K = 145.2$ $L = 152.2$

[59]

To our knowledge, the $^{19}$F NMR spectrum of 3-*H*-heptafluoro-1,4-cyclohexadiene has not previously been reported. However, the corresponding δ ($F_{vin}$) values (coefficients $K$ and $L$ at X = FH) were calculated using spectral data of 1,6-diH-hexafluoro-1,4-cyclohexadiene and the increments $a$, $b$ and $c$ of hydrogen atom taken from spectrum of 1-*H*-heptafluoro-1,4-cyclohexadiene.

The δ (F-2) values for nonafluorocyclohexenes and δ (F-1), δ (F-2) values for heptafluorocyclohexen-3-ones were predicted from Eqs. (4)–(6), respectively, which are the modified Eqs. (1)–(3).

$$\delta(F-2) = -(151.5 + a) \quad (4)$$

$$\delta(F-1) = -(135.2 + a) \quad (5)$$

$$\delta(F-2) = -(144.1 + a) \quad (6)$$

Here the value −151.5 is the δ (F-2) of the fluorine resonance in decafluorocyclohexene (V.V. Bardin, unpublished results) and values −135.2, −144.1 are the δ (F-1), δ (F-2) in octafluorocyclohexen-3-one [60].

The following accuracy of the predicted chemical shifts of vinylic fluorines $\Delta\delta(F) = (\delta_{calc} - \delta_{exp})$ was found by examination: (1) $\Delta\delta(F) \leq 1.2$ ppm for fluorinated 1,4-cyclohexadienes (for all data presented in Tables 3–5), (2) $\Delta\delta(F) \leq 1.5$ ppm for 1-R- and 2-R-pentafluoro-1,4-cyclohexadien-3-ones (R = H, Cl, Br, $CH_3$, $CF_3$, $C_6F_5$, $OCHF_2$), (3) $\Delta\delta(F) \leq 1.2$ ppm for 1-R-nonafluorocyclohexenes (all R listed in Table 8 except $NO_2$), (4) $\Delta\delta(F) \leq 1.3$ ppm for 1-R- and 2-R-heptafluorocyclohexen-3-ones (R = Cl, Br). For a few compounds the error $\Delta\delta(F)$ were found to be 2 to 2.2 ppm.

### 2.2.2. Prediction of the NMR line position for allylic fluorine atoms

Calculation of the chemical shifts of the allylic fluorine atoms depends on the mutual location of the two substituents $R_1$ and $R_2$ in the molecule.

When they belong to the other C=C bond, Eqs. (7) and (8) were used.

Table 3
Chemical shifts (in ppm) of fluorine-containing 1,4-cyclohexadienes

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| F | $CDCl_3$ | −156.5 | −156.5 | −109.5 | −156.5 | −156.5 | −109.5 | [3] |
| | $CCl_4$ | −156 | −156 | −113 | −156 | −156 | −113 | [27] |
| | $CDCl_3$ | −156.3 | −156.3 | −112.3 | −156.3 | −156.3 | −112.3 | V.V. Bardin, unpublished results |
| 1-Cl | $CCl_4$ | − | −131 | −115 | −156 (?) | −161 (?) | −108 | [27] |
| | $CCl_4$ | − | −126.9 | −110.9 | −156.9 | −151.9 | −103.9 | [28] |
| 1-Br | $CCl_4$ | − | −120.5 | −113.6 | −159.3 | −153.1 | −103.1 | [29] |
| | $CCl_4$ | − | −122 | −115 | −156 (?) | −162 (?) | −105 | [27] |
| | | − | −119.2 | −112.3 | −158.0 | −152.0 | −102.0 | [30] |
| | $CDCl_3$ | − | −119.2 | −112.3 | −157.6 | −151.4 | −102.0 | V.V. Bardin, unpublished results |
| 1-I | $CH_2Cl_2$ | − | −104.4 | −111.8 | −157.9 | −149.7 | −95.6 | [31] |
| 1-$IF_2$ | $CH_2Cl_2$ | −158.4 | −95.7 | −111.0 | −156.0 | −149.9 | −98.0 | [31] |
| 1-IFR[a] | $CH_2Cl_2$ | −137.7 (IF) | −93.4 | −111.2 | −155.5 | −149.5 | −98.2 | [31] |
| 1-H | $CCl_4$ | 5.75 (H) | −129 | −116 | −156 (?) | −161 (?) | −102 | [27] |
| | $CCl_4$ | 6.0 (H) | −129.7 | −117.3 | −161.6 | −156.9 | −104.7 | [29] |
| | $CDCl_3$ | n.d. (H) | −126.6 | −114.4 | −158.4 | −153.7 | −101.4 | [3] |
| | $CDCl_3$ | 5.92 (H) | −126.8 | −114.5 | −158.5 | −153.7 | −101.5 | V.V. Bardin, unpublished results |
| 1-$CH_3$ | $CCl_4$ | n.d. (H) | −135.9 | −113.5 | *−159.0* | *−154.4* | −106.9 | [32] |
| | | 1.60 (H) | n.d. | n.d. | n.d. | n.d. | n.d. | [4] |
| | $CFCl_3$ | 1.78 (H) | −135.9 | −113.6 | −159.6 | −154.8 | −107.8 | V.V. Bardin, unpublished results |
| 1-$CH_2F$ | | −221.8 | −127.1 | −113.9 | −158.2 | −153.4 | −105.8 | [33] [34] |
| | | 5.22 (H) | | | | | | |
| 1-$CHF_2$ | | −118.0 | −123.2 | −113.9 | −158.9 | −153.9 | −103.9 | [33] [34] |
| | | 6.53 (H) | | | | | | |
| 1-$CF_3$ | $CDCl_3$ | −59.0 | −115.3 | −113.4 | −157.9 | −152.3 | −104.2 | V.V. Bardin, unpublished results |
| 1-$C_3F_7$ | $CFCl_3$ | [b] | −109.8 | −113.3 | −158.5 | −151.7 | −102.1 | [35] |
| 1-c-$C_6F_9$ | ether | [c] | −115.1 | −112.5 | −156.7 | −151.2 | −101.4 | [36] [37] |
| 1-EtOCO | $CFCl_3$ | 1.28 ($CH_3$) | −116.5 | −112.9 | −159.9 | −153.0 | −103.2 | V.V. Bardin, unpublished results |
| | | 4.48 ($CH_2$) | | | | | | |
| 1-$C_6H_5$ | acetone | 7.5–7.7 (H) | −131.9 | −111.7 | −159.1 | −153.2 | −102.2 | [38] |
| 1-$C_6F_5$ | $CCl_4$ | n.d. | −123.9 | −115.9 | −155.9 (?) | −160.9 (?) | −106.9 | [27] |
| | $CCl_4$ | [d] | −120.5 | −113.3 | −157.5 | −152.1 | −104.0 | [6] |

(*continued*)

Table 3 (*continued*)

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | $CDCl_3$ | [d] | −120.5 | −113.3 | −157.4 | −152.0 | −103.8 | V.V. Bardin, unpublished results |
| 1-$OCH_3$ | $CCl_4$ | 4.15 (H) | −167.5 | −112.5 | −159.0 | −160.5 | −111.5 | [27] |
| | | n.d. (H) | *−168.0* | *−111.8* | *−160.9* | *−160.9* | *−111.8* | [4] |
| 1-$OCHF_2$ | $CCl_4$ | −81.6 | −144.7 | −111.6 | −157.2 | −154.5 | −108.9 | [39] |
| | $CFCl_3$ | −82.4 | −145.6 | −112.2 | −157.5 | −155.4 | −109.8 | V.V. Bardin, unpublished results |
| | | 6.77 (H) | | | | | | |
| 1-$OC_2H_5$ | $CCl_4$ | 1.42 ($CH_3$), 4.4 ($CH_2$) | *−163.3* | −110.1 | *−158.9* | *−157.1* | −110.1 | [8] |
| | | 4.3 (H) | −166.5 | −113.5 | −159.5 | −161.0 | −112.5 | [27] |
| 1-$OC_3H_7$ | $CCl_4$ | 4.15 ($OCH_2$) | −165.5 | −112.0 | −159.0 | −160.5 | −111.0 | [27] |
| 1-$OC_4H_9$ | $CCl_4$ | 4.25 ($OCH_2$) | −165.0 | −112.0 | −159.5 | −161.0 | −111.0 | [27] |
| 1-$NO_2$ | | − | −120.7 | −112.0 | −152.4 (?) | −156.6 (?) | −105.8 | [40] |
| | $CH_2Cl_2$ | − | −119.0 | −112.5 | −157.0 | −152.8 | −106.3 | [21] |
| 1-$SiMe_3$ | $CDCl_3$ | 0.34 (H) | −115.1 | −113.5 | −160.1 | −151.8 | −96.9 | [7] |
| 1-$SiMe_2C_6F_5$ | $CDCl_3$[e] | [f] | −111.7 | −113.6 | −159.2 | −151.5 | −96.6 | [7] |
| | | 0.74 (H) | | | | | | |
| 1-$SiMe_2C_6F_7$ | $CDCl_3$[e] | [g] | −110.0 | −113.7 | −159.0 | −151.4 | −96.4 | [7] |
| | | 0.70 (H) | | | | | | |
| 1-$SiFMe_2$ | $CDCl_3$[e] | −160.1 | −113.3 | −113.3 | −160.5 | −152.5 | −100.0 | [7] |
| | | 0.57 (H) | | | | | | |
| 1-$SiF_3$ | $CDCl_3$[e] | −136.0 | −103.4 | −114.6 | −158.5 | −151.7 | −97.0 | [7] |
| 1-$GeEt_3$ | $CDCl_3$[e] | 1.09–1.14 (H) | −115.3 | −113.1 | −160.0 | −151.3 | −95.7 | [7] |
| 1-$GeF_3$ | $CDCl_3$[e] | −151.4 | −99.1 | −112.6 | −155.8 | −149.6 | −94.0 | [7] |
| 1-$Xe^+$ $[AsF_6]^-$ | $CD_3CN$[h] | −1975.1 ($^{129}Xe$) | −95.8 | −110.0 | −153.0 | −147.9 | −95.8 | [38] |
| 1-$Xe^+$ $[AsF_6]^-$ | HF[h] | −2348.5 ($^{129}Xe$) | −90.6 | −107.9 | −151.5 | −147.4 | −93.6 | [38] |
| 3-Cl | neat | −161.3 | −151.2 | −117.7 | −151.2 | −161.3 | −112, −113 | [41] |
| | | *−159.7* | *−149.7* | *−116.7* | *−149.7* | *−159.7* | *−110.7, −110.9* | [42] |
| 3-Br | neat | −159.7 | −145.2 | −118.7 | −145.2 | −159.7 | −109, −112 | [43] [44] |
| | $CH_2Cl_2$ | −159.7 | −145.1 | −118 | −145.1 | −159.7 | −108.5 (A) −110.9 (B) | V.V. Bardin, unpublished results |
| 3-$CH_3$ | | *−146.7* | *−159.8* | −150.6 n.d. (H) | *−159.8* | *−146.7* | −107.3 | [4] |
| 3-$OCH_3$ | | *−155.0* | *−166.8* | −128.3 3.40 (H) | *−166.8* | *−155.0* | −112.8 | [4] |
| 3-$OCHF_2$ | | −158.0 | −154.3 | −121.9 | −154.3 | −158.0 | −112.1 | [33] [34] |

(*continued*)

Table 3 (*continued*)

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | −83.6 ($OCHF_2$) | | | | |
| | | | | 6.79 (H) | | | | |
| 3-$OCF_3$ | | −157.7 | −154.6 | −125.5 | −154.6 | −157.7 | −112.1 | [9] |
| | | | | −58.1 ($OCF_3$) | | | | |
| 3-$OC(CF_3)_3$ | | −157.4 | −152.7 | −118.1 | −152.7 | −157.4 | −114.0 | [9] |
| | | | | −70.4 ($CF_3$) | | | | |
| 3-$OTeF_5$ | | −157.5 | −156.8 | −108.4[i] | −156.8 | −157.5 | −113.6 | [45] |
| 3-$NO_2$ | $CCl_4$ | −149.2 | −152.8 | −135.4 | −152.8 | −149.2 | −110.9, −112.7 | [29] |
| 1-Br | $CH_2Cl_2$ | − | 6.58 (H) | −102.8 | −154.8 | −153.2 | −102.5 | [21] |
| 2-H | | | | | | | | |
| 1,2-$H_2$ | $CDCl_3$ | n.d. (H) | n.d. (H) | −104.7 | −156.0 | −156.0 | −104.7 | [3] |
| | $CH_2Cl_2$ | 6.28 (H) | 6.28 (H) | −104.4 | −156.0 | −156.0 | −104.4 | [21] |
| 1-$CHF_2$ | $CCl_4$ | −121.3 | 6.62 (H) | −108.1 | −156.2 | −156.2 | −105.4 | [16] |
| 2-H | | 6.45 (H) | | | | | | |
| 1,2-$(CF_3)_2$ | | −58.2 | −58.2 | −105.0 | −156.5 | −156.5 | −105.0 | [20] |
| 1-$C_6H_5$ | acetone | 7.60 (H) | 6.75 (H) | −102.3 | −157.6 | −156.4 | −103.2 | [46] |
| 2-H | | | | | | | | |
| 1-$NO_2$ | $CH_2Cl_2$ | − | 6.55 (H) | −104.1 | −155.4 | −154.8 | −109.0 | [21] |
| 2-H | | | | 3.40 (H) | | | | |

[a]R = $OCOCF_3$, at −10°C.
[b]δ (F): −109.8 (α-$CF_2$), −126.0 (β-$CF_2$), −79.1 ($CF_3$).
[c]Perfluorocyclohexen-1-yl; δ (F): −110.4 (F-2′), −119.2 (F-3′,3′), −133.3 (F-4′,4′,5′,5′), −107.4 (F-6′,6′).
[d]δ (F) ($C_6F_5$): −137.0 (*ortho*), −160.3 (*meta*), −148.6 (*para*) [6]; −137.4 (*ortho*), −160.3 (*meta*), −148.6 (*para*) (V.V. Bardin, unpublished results).
[e]At 45°C.
[f]δ (F) ($C_6F_5$): −127.6 (*ortho*), −161.2 (*meta*), −149.8 (*para*).
[g]Perfluoro-1,4-cyclohexadien-1-yl.
[h]At −30°C.
[i]δ (F) (F–Te): −40.0 and −49.0.
[j]δ (F) ($C_6F_5$): −137.3 (*ortho*), −160.2 (*meta*), −148.5 (*para*).
[k]δ (F) ($C_6F_5$): −151.9 (*ortho*), −163.3 (*meta*), −158.3 (*para*).
n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
−*123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

Table 4
Chemical shifts (in ppm) of fluorine-containing 1,4-cyclohexadienes

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1-$SiMe_3$ 2-H | $CH_2Cl_2$ | 0.30 (H) | 6.36 (H) | −103.1 | −157.0 | −153.5 | −97.8 | [47] |
| 1-Cl 3-$NO_2$ | $CCl_4$ | – | −124.8 | −133.7 | −153.7 | −146.0 | −104.4, −105.6 | [29] |
| 1-Br 3-$NO_2$ | $CCl_4$ | – | −116.5 | −133.7 | −154.0 | −145.4 | −101.0, −102.2 | [29] |
| 1-H 3-$NO_2$ | $CCl_4$ | 6.3 (H) | −123.0 | −135.6 | −154.6 | −148.0 | −100.3, −102.1 | [29] |
| 1-$CH_3$ 3-$NO_2$ | $CCl_4$ | 2.1 (H) | −131.8 | −134.7 | −155.1 | −148.2 | −104.7, −106.5 | [32] |
| 1-H 3-Cl | neat | 5.56 (H) | −119.2 | −117.7 | −150.6 | −156.9 | −97.4 | V.V. Bardin, unpublished results |
| 1-Cl 4-H | $CCl_4$ | – | −124.9 | −100.7 | 5.89 (H) | −122.6 | −107.5 | [48] |
| 1-Cl 4-$CH_3$ | $CCl_4$ | – | −125.3 | −105.3* | 2.00 (H) | −131.3 | −107.3* | [48] |
| 1-Br 4-$CH_3$ | $CCl_4$ | – | −116.2 | −105.9 | 2.04 (H) | −129.9 | −102.1 | [48] |
| 1-Br 4-H | $CCl_4$ | – | −115.9 | −103.6 | 5.91 (H) | −121.5 | −100.6 | [48] |
| | $CH_2Cl_2$ | – | −116.1 | −103.6 | 6.04 (H) | −121.8 | −100.6 | [21] |
| 1-$CH_3$ 4-H | $CCl_4$ | 1.92 (H) | −132.7 | −101.7 | 5.66 (H) | −124.2 | −108.8 | [48] |
| 1-$CF_3$ 4-H | | −59.2 | −113.3 | −101.7 | 6.01 (H) | −123.2 | −106.1 | [19] |
| 1-$SiMe_3$ 4-H | $CH_2Cl_2$ | 0.36 (H) | −112.4 | −101.0 | 5.92 (H) | −122.5 | 97.8 | [47] |
| 1,4-$H_2$ | $CCl_4$ | 5.87 (H) | −124.4 | −103.1 | 5.87 (H) | −124.4 | −103.1 | [49] |
| | $CDCl_3$ | n.d. (H) | −124.5 | −103.1 | n.d. (H) | −124.5 | −103.1 | [3] |
| | | 5.90 (H) | −124.5 | −102.7 | 5.90 (H) | −124.5 | −102.7 | [21] |
| 1,4-$(CH_3)_2$ | $CCl_4$ | n.d. (H) | −133.1 | −106.7 | n.d. (H) | −133.1 | −106.7 | [48] |
| 1,4-$(CF_3)_2$ | | −59.3 | −112.6 | −105.0 | −59.3 | −112.6 | −105.0 | [19] |
| | | −59.1 | −112.3 | −104.6 | −59.1 | −112.3 | −104.6 | [20] |
| 1,5-$Cl_2$ | $CCl_4$ | – | −128 | −111 | −128 | – | −97 | [28] |
| 1-Br 5-H | $CH_2Cl_2$ | – | −120.5 | −114.7 | −128.3 | 6.19 (H) | −89.8 | [21] |
| 1,5-$H_2$ | $CDCl_3$ | n.d. (H) | −129.4 | −118.5 | −129.4 | n.d. (H) | −89.3 | [3] |
| | $CH_2Cl_2$ | 6.07 (H) | −129.3 | −118.0 | −129.3 | 6.07 (H) | −89.1 | [21] |
| 1-$CF_3$ 5-H | $CH_2Cl_2$ | −58.9 | −117.0 | −116.8 | −128.5 | 6.12 (H) | −91.6 | [21] |
| 1-$CF_3$ 5-$NO_2$ | ether | −58.1 | −108.3 | −112.4 | – | −120.2 | −116.2 | V.V. Bardin, unpublished results |

(*continued*)

Table 4 (*continued*)

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1,5-$(C_6F_5)_2$ | $CCl_4$ | j | −120.5 | −113.6 | −120.5 | j | −92.9 | [18] |
| 1-$SiMe_3$ | $CH_2Cl_2$ | 0.35 (H) | −117.1 | −117.1 | −131.4 | 6.06 (H) | 83.4 | [47] |
| 5-H | | | | | | | | |
| 1,6-$Cl_2$ | $CDCl_3$ | – | −129.5 | −109.7 | −159.7 | −143.4 | −110.8 | [10] |
| 1-Cl | $CCl_4$ | – | −120.6 | −111.1, −112.3 | −150.3 | −148.9 | −128.5 | [29] |
| 6-$NO_2$ | | | | | | | | |
| 1-Br | $CCl_4$ | – | −111.1 or −112.3 | −112.3 or −111.1 | −147.9 or −150.7 | −150.7 or −147.9 | −125.2 | [29] |
| 6-$NO_2$ | | | | | | | | |
| 1,6-$H_2$ | $CH_2Cl_2$ | 5.95 (H) | −129.4 | −109.7(A) −111.0(B) | −161.3 | −140.1 | −186.7 7.00 (H) | [21] |
| 1-$NO_2$ | $CH_2Cl_2$ | – | −120.0 | −108.4 | −158.7 | −139.2 | −187.9 | [21] |
| 6-H | | | | | | | | |
| 1-$OCHF_2$ | $CCl_4$ | −82.6 | −139.1 | −112.1, −110.7 | −150.2 | −151.4 | −133.3 | [39] |
| 6-$NO_2$ | | | | | | | | |
| 1-$OC_6F_5$ | $CCl_4$ | n.d. (H) | −148.4 | −109.5 | −148.9 | −150.8 | −130.7 | [39] |
| 6-$NO_2$ | | | | | | | | |
| 3,6-$Cl_2$ | neat | −151.4 | −151.4 | −114.1, −112.1 | −151.4 | −151.4 | −114.1, −112.1 | [41] |
| | | −150.4 | −150.4 | −111.0 | −150.4 | −150.4 | −111.0 | [50] |
| | | −151.6 | −151.6 | −112.5 | −151.6 | −151.6 | −112.5 | [10] |
| 3-Cl | | −145.7 | −150.3 | −112.6 | −150.3 | −145.7 | −108.6 | [50] |
| 6-Br | | | | | | | | |
| 3-Cl | | −155.0 | −146.6 | −113.3 | −146.6 | −155.0 | −115.7, 4.2 (H) | [50] |
| 6-$OSO_3Me$ | | | | | | | | |
| 3-Cl | | −156.2 | −148.8 | −113.6 | −148.8 | −156.2 | −116.9, 1.78 ($CH_3$), 4.82 ($CH_2$) | [50] |
| 6-$OSO_3Et$ | | | | | | | | |
| 3-$NO_2$ | $CCl_4$ | −148.4 | −156.1 | −136.4, −137.0 (*Z*,*E*) | −156.1 | −148.4 | −122.4, −124.5 (*Z*,*E*), −85.9 ($OCHF_2$) | [39] |
| 6-$OCHF_2$ | | | | | | | | |
| 3-$NO_2$ | $CCl_4$ | −144.6 | −152.4 | −133.8, −132.0 | −152.4 | −144.6 | −120.3, −118.2 | [39] |
| 6-$OC_6F_5$ | | | | | | | | |
| 1,2,4-$H_3$ | $CDCl_3$ | n.d. (H) | n.d. (H) | −92.5 | n.d. (H) | −125.5 | −108.4 | [17] |
| | $CDCl_3$ | 6.26 (H) | 6.26 (H) | −92.2 | 5.90 (H) | −125.6 | −108.1 | [51] |
| 1-$CF_3$ | | −64.6 | 6.83 (H) | −92.1 | 6.01 (H) | −124.7 | −110.7 | [19] |
| 2,4-$H_2$ | | | | | | | | |
| 1-$CHF_2$ | $CCl_4$ | −121.1, 6.44 (H) | 6.67 (H) | −95.5 | 6.00 (H) | −126.2 | −108.4 | [16] |
| 2,4-$H_2$ | | | | | | | | |
| 1-$CHF_2$ | $CCl_4$ | −121.1, 6.44 (H) | 6.97 (H) | −111.5 | −126.2 | 6.00 (H) | −92.6 | [16] |
| 2,5-$H_2$ | | | | | | | | |
| 1-$CH_3$ | $CCl_4$ | 2.12 (H) | −126.7 or −128.1 | −128.1 or −126.7 | – | −119.3 | −104.7, −105.7 | [48] |
| 3-$NO_2$ | | | | | | | | |
| 4-Cl | | | | | | | | |

(*continued*)

Table 4 (*continued*)

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1-$CH_3$<br>3-$NO_2$<br>4-Br | $CCl_4$ | 2.04 (H) | −126.7 | −123.8 | – | −110.9 | −105.1, −106.1 | [48] |

[a]R = $OCOCF_3$, at −10°C.
[b]δ (F): −109.8 (α-$CF_2$), −126.0 (β-$CF_2$), −79.1 ($CF_3$).
[c]Perfluorocyclohexen-1-yl; δ (F): −110.4 (F-2′), −119.2 (F-3′,3′), −133.3 (F-4′,4′,5′,5′), −107.4 (F-6′,6′).
[d]δ (F) ($C_6F_5$): −137.0 (*ortho*), −160.3 (*meta*), −148.6 (*para*) [6]; −137.4 (*ortho*), −160.3 (*meta*), −148.6 (*para*) (V.V. Bardin, unpublished results).
[e]At 45°C.
[f]δ (F) ($C_6F_5$): −127.6 (*ortho*), −161.2 (*meta*), −149.8 (*para*).
[g]Perfluoro-1,4-cyclohexadien-1-yl.
[h]At −30°C.
[i]δ (F) (F–Te): −40.0 and −49.0.
[j]δ (F) ($C_6F_5$): −137.3 (*ortho*), −160.2 (*meta*), −148.5 (*para*).
[k]δ (F) ($C_6F_5$): −151.9 (*ortho*), −163.3 (*meta*), −158.3 (*para*).
n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
*−123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

Table 5
Chemical shifts (in ppm) of fluorine-containing 1,4-cyclohexadienes

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1,4-$(CH_3)_2$ 3-$NO_2$ | $CCl_4$ | 1.99 (H) | −128.5 or −130.0 | −130.0 or −128.5 | 1.88 (H) | −126.7 | −106.2, −107.2 | [48] |
| 1-H 3-$NO_2$ 4-Cl | $CCl_4$ | 6.22 (H) | −118.3 or −119.7 | −128.1 | – | −119.7 or −118.3 | −99.5, −100.5 | [48] |
| 1-H 3-$NO_2$ 4-Br | $CCl_4$ | 6.22 (H) | −117.9 | −124.4 | – | −110.3 | −99.3, −100.3 | [48] |
| 1-H 3-$NO_2$ 4-$CH_3$ | $CCl_4$ | 6.15 (H) | −120.6 | −130.4 | 1.88 (H) | −126.9 | −100.8, −101.8 | [48] |
| 1,4-$H_2$ 3-$NO_2$ | $CCl_4$ | 6.2 (H) | −120.0 | −125.7 | 5.9 (H) | −118.7 | −102.4, −101.4 | [52] |
| 1,3,5-$H_3$ | $CDCl_3$ | n.d. (H) | −114.2 | −196.7 n.d. (H) | −114.2 | n.d. (H) | −84.8 | [17] |
| 1,5,6-$H_3$ | $CDCl_3$ | n.d. (H) | −131.5 | −114.0 | −131.5 | n.d. (H) | −179.1 n.d. (H) | [17] |
| 3-Cl 6,6-$(OMe)_2$ | | *−154.3* | *−149.9* | *−109.4* | *−149.9* | *−154.3* | 4.24 (H) | [42] |
| 3-Cl 6,6-$(OEt)_2$ | | *−153.4* | *−148.8* | *−108.1* | *−148.8* | *−153.4* | 1.28 ($CH_3$), 3.60 ($CH_2$) | [42] |
| 3-Cl 6,6-$(OPr^i)_2$ | | *−155.6* | *−148.3* | *−108.3* | *−148.3* | *−155.6* | 1.13 ($CH_3$), 4.03 (CH) | [42] |
| 3-OH 3-Bu 6-$OC_6F_5$ | | −163.6 | −148.2 | n.d. (H) | −148.2 | −163.6 | −114.4 (F) [k] | [53] |
| 1,2,4,5-$H_4$ | hexane | 5.75 (H) | 5.75 (H) | −91.6 | 5.75 (H) | 5.75 (H) | −91.6 | [54] |
| | hexane | n.d. (H) | n.d. (H) | −96.5 | n.d. (H) | n.d. (H) | −96.5 | [23] |
| | $CDCl_3$ | 6.30 (H) | 6.30 (H) | −96.7 | 6.30 (H) | 6.30 (H) | −96.7 | [51] |
| 1-Cl 2,4,5-$H_3$ | | – | n.d. (H) 6.42 (H) | −93.3 −93.5 | n.d. (H) 6.34 (H) | n.d. (H) 6.34 (H) | −99.9 −100.2 | [55] [51] |
| 1-Br 2,4,5-$H_3$ | $CDCl_3$ | – | 6.66 (H) | −94.0 | 6.36 (H) | 6.36 (H) | −96.5 | [51] |
| 1-$CHF_2$ 2,4,5-$H_3$ | $CCl_4$ | −121.2 6.41 (H) | 6.65 (H) | −99.8 | 6.34 (H) | 6.34 (H) | −96.5 | [16] |
| 1-$CF_3$ | $CDCl_3$ | −65.7 | n.d. (H) | −96.9 | n.d. (H) | n.d. (H) | −99.8 | [26] |
| 2,4,5-$H_3$ | $CCl_4$ | −64.0 | 6.78 (H) | −99.0 | 6.35 (H) | 6.35 (H) | −96.0 | [16] |
| 1-$CH_3CO$ 2,4,5-$H_3$ | $CDCl_3$ | 2.52 (H) | 6.98 (H) | −96.8* | 6.33 (H) | 6.33 (H) | −95.3* | [56] |
| 1-$NO_2$ 2,4,5-$H_3$ | $CDCl_3$ | – | 7.30–7.68 (1H) | −104.6* | 6.25–6.53 (2H) | | −101.4* | [56] |
| 1-$SiMe_3$ 2,4,5-$H_3$ | $CH_2Cl_2$ | 0.30 (H) | * | −95.6 | 6.3–6.5 (3 H)* | | −90.1 | [47] |
| 1,5-$(CF_3)_2$ | | −65.6 | 6.85 (H) | −97.0 | 6.85 (H) | −65.6 | −102.0 | [57] |

(*continued*)

Table 5 (*continued*)

| Substituent | Solvent | δ (1) | δ (2) | δ (3) | δ (4) | δ (5) | δ (6) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 2,4-$H_2$ | | | | | | | | |
| 1,2,5-$H_3$ | | n.d. (H) | n.d. (H) | −105.2 | −130.3 | n.d. (H) | −99.0 | [55] |
| 6-Cl | | | | | | | | |
| 1,3,4,5-$H_4$ | $CDCl_3$ | n.d. (H) | −110.9 | −190.6<br>n.d. (H) | n.d. (H) | n.d. (H) | −86.8, −85.4 | [17] |
| 1,4,5,6-$H_4$ | hexane | n.d. (H) | −129.7 | −103.2(A)<br>−99.3 (B) | n.d. (H) | n.d. (H) | −179.2<br>n.d. (H) | [23] |
| | $CDCl_3$ | n.d. (H) | −130.2 | −102.5(A)<br>−100.9(B) | n.d. (H) | n.d. (H) | −179.9<br>n.d. (H) | [17] |
| 3,3,4,4-$(OCH_3)_4$ | | −152.4 | −152.4 | 3.23 (H) | −152.4 | −152.4 | 3.23 (H) | [50] |
| 1-Cl<br>2,3,4,5-$H_4$ | | − | n.d. (H) | −178.8 | n.d. (H) | n.d. (H) | −91.5 (A)<br>−94.8 (B) | [55] |
| 1-$CF_3$<br>2,3,4,5-$H_4$ | $CDCl_3$ | −65.1 | n.d. (H) | −185.0<br>n.d. (H) | n.d. (H) | n.d. (H) | −87.8, −97.1 | [26] |
| 1-$CF_3$<br>2,4,5,6-$H_4$ | $CDCl_3$ | −68.0 | n.d. (H) | −87.6, −91.9 | n.d. (H) | n.d. (H) | −185.2<br>n.d. (H) | [26] |
| 1,3-$(CF_3)_2$<br>2,4,5-$H_3$ | | −65.3 | 7.65 (H) | −164.2(F)<br>−79.9 ($CF_3$) | 6.80 (H) | 6.40 (H) | −92.7 (6A)<br>−99.7 (6B) | [57] |
| 1,2,4,5-$H_4$<br>3-Cl | | n.d. (H) | n.d. (H) | −104.0 | n.d. (H) | n.d. (H) | −93.2 | [55] |
| 1,2,4,5-$H_4$<br>3-$C_6H_5$ | $CCl_4$ | n.d. (H) | n.d. (H) | −152.0 | n.d. (H) | n.d. (H) | −84.7, −90.5 | [58] |
| 1,2,3,5,6-$(CF_3)_5$ | | −73.6 | −73.6 | −172.1, −64.3 ($CF_3$) | −79.3 | −73.6 | −169.9, −64.3 ($CF_3$) | [25] |
| 1,2,4,5,6-$H_5$ | hexane | n.d. (H) | n.d. (H) | −91.1 (A), −85.1 (B) | n.d. (H) | n.d. (H) | −181.8 | [23] |
| 1,2,3,4,5,6-$H_6$ (*Z*) | hexane | n.d. (H) | n.d. (H) | −174.4<br>n.d. (H) | n.d. (H) | n.d. (H) | n.d. (H)<br>−174.4<br>n.d. (H) | [23] |

[a]R = $OCOCF_3$, at −10°C.
[b]δ (F): −109.8 (α-$CF_2$), −126.0 (β-$CF_2$), −79.1 ($CF_3$).
[c]Perfluorocyclohexen-1-yl; δ (F): −110.4 (F-2′), −119.2 (F-3′,3′), −133.3 (F-4′,4′,5′,5′), −107.4 (F-6′,6′).
[d]δ (F) ($C_6F_5$): −137.0 (*ortho*), −160.3 (*meta*), −148.6 (*para*) [6]; −137.4 (*ortho*), −160.3 (*meta*), −148.6 (*para*) (V.V. Bardin, unpublished results).
[e]At 45°C.
[f]δ (F) ($C_6F_5$): −127.6 (*ortho*), −161.2 (*meta*), −149.8 (*para*).
[g]Perfluoro-1,4-cyclohexadien-1-yl.
[h]At −30°C.
[i]δ (F) (F–Tc): −40.0 and −49.0.
[j]δ (F) ($C_6F_5$): −137.3 (*ortho*), −160.2 (*meta*), −148.5 (*para*).
[k]δ (F) ($C_6F_5$): −151.9 (*ortho*), −163.3 (*meta*), −158.3 (*para*).
n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
*−123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

Table 6
Coupling constants of fluorine-containing 1,4-cyclohexadienes

| Substituent | Solvent | J, Hz | Ref. |
|---|---|---|---|
| 1-Cl | $CCl_4$ | (2, 3) 24, (2, 4) 3.0, (2, 6) 10.5, (3, 4) 21.5, (3, 5) 10.5, (3, 6) 5.25, (4, 5) 6.0, (4, 6) 10.5, (5, 6) 22.5. | [27] |
| | $CCl_4$ | (2, 3) 21, (2, 5) 3, (2, 6) 10, (3, 4) 19, (3, 5) 10, (3, 6) 5, (4, 5) 4, (4, 6) 9.5, (5, 6) 21 | [28] |
| 1-Br | $CCl_4$ | (2, 3) 24.0, (2, 4) 3.0, (2, 6) 11.5, (3, 4) 20.0, (3, 5) 12.0, (3, 6) 6.0, (4, 5) 6.0, (4, 6) 11.5, (5, 6) 24.0. | [27] |
| | $CDCl_3$ | (2, 3) 19, (2, 6) 14, (3, 4) 22, (3, 5) 9, (3, 6) 5, (4, 5) 5, (4, 6) 10, (5, 6) 22. | V.V. Bardin, unpublished results |
| 1-I | $CH_2Cl_2$ | (2, 3) 24.3, (2, 4) 0, (2, 5) 2.7, (2, 6) 10.2, (3, 4) 19.6, (3, 5) 10.6, (3, 6) 4.6, (4, 5) 4.5, (4, 6) 10.3, (5, 6) 23.1 | [31] |
| 1-H | $CCl_4$ | (2, 1) 10.5, (2, 3) 21.0, (2, 4) 2.0, (2, 6) 10.5, (3, 1) 2, (3, 4) 21.1, (3, 5) 10.5, (3, 6) 5.25, (4, 5) 6.0, (4, 6) 10.5, (5, 6) 21.0, (6, 1) 2. | [27] |
| | $CDCl_3$ | (2, 1) 10.4, (2, 3) 20.8, (2, 5) 1.4, (2, 6) 10.4, (3, 1) 1.9, (3, 4) 19.5, (3, 5) 10.7, (3, 6) 5.3, (4, 5) 4.5, (4, 6) 10.1, (5, 6) 20.1, (6, 1) 5.3 | V.V. Bardin, unpublished results |
| 1-$CH_3$ | $CCl_4$ | (2, 3) ≈ (3, 4) ≈ (5, 6) ≈ 20–22, (2, 6) ≈ (4, 6) ≈ (3, 5) ≈ 10–11, (3, 6) 5.5, (6, 1) 2.5 | [32] |
| 1-$CH_2F$ | $CFCl_3$ | (FCH) 46, (FC, 2) 6, (FC, 3) 2, (FC, 6) 4, (2, 3) 22, (2, 6) 8, (3, 4) 19, (3, 5) 11, (3, 6) 5, (4, 5) 4.5, (4, 6) 10.5, (5, 6) 20 | V.V. Bardin, unpublished results |
| 1-$CHF_2$ | $CFCl_3$ | ($F_2CH$) 54, (F2C, 2) 11, ($F_2C$, 6) 5, (2, 3) 21, (2, 5) 2, (2, 6) 11, (3, 4) 20, (3, 5) 10, (3, 6) 5, (4, 5) 4.5, (4, 6) 10, (5, 6) 20 | V.V. Bardin, unpublished results |
| 1-$CF_3$ | $CDCl_3$ | ($F_3C$, 2) 18.4, ($F_3C$, 6) 8.0, (2, 3) 21, (2, 6) 11, (3, 4) 20, (3, 5) 10, (4, 5) 5.7, (4, 6) 10, (5, 6) 20.0 | V.V. Bardin, unpublished results |
| 1-EtOCO | $CFCl_3$ | (2, 3) 22, (2, 6) 10, (3, 4) 20, (3, 5) 11, (3, 6) 4, (4, 5) 5.5, (4, 6) 10.5, (5, 6) 22 | V.V. Bardin, unpublished results |
| 1-$C_6H_5$ | acetone | (2, 3) 22.4, (2, 4) < 1.5, (2, 5) < 1.5, (2, 6) 10.2, (3, 4) 19.4, (3, 5) 10.2, (3, 6) 6, (4, 5) 6, (4, 6) 10.2, (5, 6) 20.9 | [38] |
| 1-$C_6F_5$ | $CCl_4$ | (2, 3) 22.5, (2, 4) 3, (2, 6) 11.3, (3, 4) 22.5, (3, 5) 11.3, (3, 6) 5.5, (4, 5) 5.5, (4, 6) 11.3, (5, 6) 22.5. | [27] |
| | $CDCl_3$ | (2, 3) 21.5, (2, 6) 10.5, (3, 4) 19, (3, 5) 10, (3, 6) 5, (4, 5) 5, (4, 6) 10, (5, 6) 21 | V.V. Bardin, unpublished results |
| 1-$OCHF_2$ | $CCl_4$ | ($F_2CH$) 75, (2, 3) 20, (2, 6) 10, (3, 4) 20, (3, 5) 10, (3, 6) 5, (4, 5) 4.5, (4, 6) 10, (5, 6) 20. | [39] |
| | $CFCl_3$ | ($F_2CH$) 75, ($F_2CO$, 2) 13, ($F_2CO$, 6) 4.2, (2, 3) 22, (2, 6) 10, (3, 4) 20, (3, 5) 10, (3, 6) 5, (4, 5) 5, (4, 6) 10.5, (5, 6) 20 | V.V. Bardin, unpublished results |
| 1-$NO_2$ | | (2, 3) ≈ (3, 4) 21, (2, 6) ≈ (3, 5) ≈ (4, 6) 10, (4, 5) 5, (5, 6) 20. | [40] |
| | $CH_2Cl_2$ | (2, 3) 22.3, (2, 5) 3.0, (2, 6) 9.5, (3, 4) 20.3, (3, 5) 10.6, (3, 6) 3.7, (4, 5) 5, (4, 6) 9.7, (5, 6) 21 | [21] |
| 1-$SiMe_3$ | $CDCl_3$ | (2, 3) 23.5, (2, 4) 2, (2, 6) 10, (3, 4) 18, (3, 5) 11, (3, 6) 5, (4, 5) 5, (4, 6) 11, (5, 6) 22 | [7] |
| 1-$SiMe_2C_6F_5$ | $CDCl_3$[b] | (2, 3) 23.5, (2, 6) 10, (3, 4) 19, (3, 5) 11, (3, 6) 5, (4, 5) 5, (4, 6) 11, (5, 6) 22 | [7] |
| 1-$SiMe_2C_6F_7$[a] | $CDCl_3$[b] | (2, 3) 25, (2, 4) 2, (3, 4) 19, (3, 5) 11, (3, 6) 5, (4, 5) 5, (5, 6) 21 | [7] |
| 1-$SiFMe_2$ | $CDCl_3$[b] | (2, 4) 1.5, (2, 6) 10, (3, 4) 19, (3, 5) 11, (3, 6) 4.5, (4, 6) 11, (5, 6) 22, (FSiCH) 7.5 | [7] |
| 1-$SiF_3$ | $CDCl_3$[b] | (2, 3) 22.5, (2, 4) 2, (2, 5) 1.5, (2, 6) 10.5, (3, 4) 20, (3, 5) 11, (3, 6) 4.5, (4, 5) 4.5, (4, 6) 10, (5, 6) 21 | [7] |
| 1-$GeEt_3$ | $CDCl_3$[b] | (2, 3) 25, (2, 4) 2, (2, 5) 1, (2, 6) 10, (3, 4) 19, (3, 5) 11, (3, 6) 5, (4, 5) 5, (4, 6) 11, (5, 6) 23 | [7] |
| 1-$GeF_3$ | $CDCl_3$[b] | (2, 3) 22, (2, 4) 1.5, (2, 5) 1.5, (2, 6) 10, (3, 4) 20, (3, 5) 11, (3, 6) 4, (4, 5) 3.5, (4, 6) 10, (5, 6) 21 | [7] |
| 1-$Xe^+$ [$AsF_6$] | $CD_3CN$[c] | (2, 3) 20, (3, 4) 20.5, (3, 5) 12, (3, 6) < 1, (4, 5) 3.6, (4, 6) 9.4, (5, 6) 26.8, $^3J$(Xe)–(F-2) 82.1 ± 1.1 | [38] |
| 1-$Xe^+$ [$AsF_6$]$^-$ | HF[c] | (2, 3) 21.9, (2, 4) < 1, (2, 5) 3.6, (2, 6) 8.6, (3, 4) 19.4, (3, 5) 9.6, (3, 6) 3.5, (4, 5) < 1, (4, 6) 9,5, (5, 6) 21.4, (2, $^{129}$Xe) 70.6 ± 1.1, ($^{129}$Xe)–(F-2) 68.5 ± 1.1. | [38] |
| 3-Cl | neat | (1, 3) 6, (1, 6) 20, (2, 3) 24, (2, 6) 10 | [41] |
| 3-Br | neat | (6A, 6B) 300. | [43,44] |
| | $CH_2Cl_2$ | (1, 2) 5, (1, 3) 8.2, (1, 4) 2.8, (1, 6) 20.0, (2, 3) 25.0, (2, 6) 9.9, (3, 6) 5.6 | V.V. Bardin, unpublished results |
| 3-$OCHF_2$ | | (1, 2) 3.6, (1, 3) 8.6, (1, 6) 20, (1, $OCHF_2$) 5.5, (2, 3) 22.5, (2, 6) 10.5, (2, $OCHF_2$) 5, (3, 6) 6, ($F_2CH$) 73 | [33,34] |
| 3-$OTeF_5$ | | (1, 6) 18.3, (F, $^{125}$Te) 3760–3790 | [45] |

(*continued*)

Table 6 (*continued*)

| Substituent | Solvent | J, Hz | Ref. |
|---|---|---|---|
| 1-Br<br>2-H | $CH_2Cl_2$ | (2, 3) 6, (2, 4) 5, (2, 6) 5, (3, 4) 19, (3, 5) 11, (3, 6) 5, (4, 5) 6, (4, 6) 12, (5, 6) 22 | [21] |
| 1,2-$H_2$ | $CH_2Cl_2$ | (1, 6) 7, (2, 3) 7, (3, 4) 23, (3, 5) 12, (4, 6) 12, (5, 6) 23, (3, 6) 2.5 [d], (4, 5) 6[d] | [21] |
| 1-$CHF_2$<br>2-H | | ($F_2CH$) 53.9 | [16] |
| 1-$C_6H_5$<br>2-H | acetone | (3A, 3B) 300, (3A, 2) 6.3, (3B, 2) 6.3, (3, 4) 19.9, (3, 5) 11.2, (3A, 6A) 7.65, (3A, 6B) 4.1, (3B, 6A) 4.3, (3B, 6B) 7.0, (4, 2) 7.3, (4, 5) 6.3, (4, 6) 11.6, (5, 2) 0.8, (5, 6) 21.0, (6A, 6B) 300, (6, 2) 1.8 | [46] |
| 1-$NO_2$<br>2-H | $CH_2Cl_2$ | (2, 3) 5, (2, 6) 2, (3, 4) 21, (3, 6) 3.8, (4, 5) 4.4, (4, 6) 10.6, (5, 6) 20.6 | [21] |
| 1-$SiMe_3$<br>2-H | $CH_2Cl_2$ | (2, 3) 4.7, (2, 4) 7.5, (3, 4) 19.4, (3, 5) 11.2, (3, 6) 6.2, (4, 5) 6.3, (4, 6) 12.1, (5, 6) 21.5 | [47] |
| 1-$CH_3$<br>3-$NO_2$ | $CCl_4$ | (1, 2) 3.5, (1, 6) 3.5, (2, 3) 23, (2, 6) 9, (3, 4) 21–23, (4, 6) 10.5, (5, 6) 21 | [32] |
| 1-Br<br>4-H | $CH_2Cl_2$ | (2, 3) 22, (2, 4) 6.7, (2, 6) 11, (3, 4) 5, (3, 5) 11, (3, 6) 5, (4, 5) 10.5, (4, 6) 5, (5, 6) 22 | [21] |
| 1-$CF_3$<br>4-H | | (2, $CF_3$) 17.9, (2, 3) 21.6, (3, $CF_3$) 0.95, (5, 4) 11.3, (6, $CF_3$) 7.5 | [19] |
| 1-$SiMe_3$<br>4-H | $CH_2Cl_2$ | (2, 3) 23, (2, 4) 8, (2, 6) 11, (3, 4) 5, (3, 5)11, (3, 6) 5, (4, 5) 10, (4, 6) 2.5, (5, 6) 22 | [47] |
| 1,4-$H_2$ | $CH_2Cl_2$ | (1, 2) 10, (1, 6) 5, (2, 3) 22, (2, 4) 5, (2, 6) 11, (3, 4) 5, (3, 5) 11, (3, 6) 5[d], (4, 5) 10, (4, 6) 5, (5, 6) 22 | [21] |

[a]Perfluoro-1,4-cyclohexadien-1-yl.
[b]At 45°C.
[c]At −30°C.
[d]Apparent constant.
n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
*−123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

Table 7
Coupling constants of fluorine-containing 1,4-cyclohexadienes

| Substituent | Solvent | J, Hz | Ref. |
|---|---|---|---|
| 1,4-$(CF_3)_2$ | | ($F_3C$, 2) 18.8, ($F_3C$, 6) 6.6, (2, 3) 9.4 (?). | [19] |
| 1,5-$Cl_2$ | $CCl_4$ | (2, 3) 22, (2, 6) 10, (3, 6) 4 | [28] |
| 1-Br 5-H | $CH_2Cl_2$ | (2, 3) 23, (2, 6) 10, (3, 4) 21, (3, 5) 1.8, (3, 6) 4, (4, 5) 10, (4, 6) 10, (5, 6) 4 | [21] |
| 1,5-$H_2$ | $CH_2Cl_2$ | (1, 2) 11, (1, 6) 5, (2, 3) 20.5, (2, 6) 11, (3, 4) 20.5, (3, 6) 5, (4, 5) 11, (4, 6) 11, (5, 6) 5 | [21] |
| 1-$CF_3$ 5-H | $CH_2Cl_2$ | (2, $CF_3$) 19, (3, 4) 20, (4, 5) 10, (4, 6) 10, (5, 6) 5.5, (6, $CF_3$) 8 | [21] |
| 1-$CF_3$ 5-$NO_2$ | ether | (2, $CF_3$) 18, (2, 3) 22, (2, 6) 12, (3, 5) 11, (3, 6) 2, (5, 6) 22, (6, $CF_3$) 7.5 | V.V. Bardin, unpublished results |
| 1-$SiMe_3$ 5-H | $CH_2Cl_2$ | (4, 5) 10.5, (5, 6) 5 | [47] |
| 1,6-$Cl_2$ | $CDCl_3$ | (2, 3) 24, (2, 4) 1.5, (2, 5) 3, (2, 6) 5, (3, 4) 20, (3, 5) 10, (3, 6) 5, (4, 5) 5, (4, 6) 5, (5, 6) 25 | [10] |
| 1,6-$H_2$ | $CH_2Cl_2$ | (1, 2) 11, (1, 3) 7, (1, 6F) 6, (2, 3) 21, (2, 6F) 7, (2, 6H) 4, (3, 4) 19, (3, 5) 15, (3, 6F) 5, (4, 5) 6, (4, 6F) 7, (5, 6) 28, (6F, 6H) 48 | [21] |
| 1-$NO_2$ 6-H | $CH_2Cl_2$ | (2, 6F) 7.2, (3, 4) 20, (3, 5) 6.4, (3, 6F) 2, (4, 5) 10.5, (4, 6F) 9.8, (4, 6H) 4.5, (5, 6F) 31, (5, 6H) 12, (6F, 6H) 48.5 | [21] |
| 1-$OCHF_2$ 6-$NO_2$ | $CCl_4$ | (2, $OCHF_2$) 15.5, (2, 3) 21, (2, 6) 6, (3, 5) 9.5, (3, 4) 21, (4, 6) 6, (5, 6) 22.5, ($F_2CH$) 74 | [39] |
| 3,6-$Cl_2$ | neat | (1, 3) 11, (1, 6) 19. | [41] |
| | | (1, 3) 11, (1, 6) 19 | [50] |
| 3-Cl 6-$OSO_2OEt$ | | (HH) 8 | [50] |
| 3-$NO_2$ 6-$OCHF_2$ | | (1, 3) 9, (1, 6) 22, (2, 3) 22, (2, 6) 6, ($F_2CH$) 72 | [39] |
| 3-$NO_2$ 6-$OC_6F_5$ | $CCl_4$ | (1, 3) 6, (1, 6) 21–22, (2, 3) 21–22, (2, 6) 9 | [39] |
| 1,2,4-$H_3$ | $CDCl_3$ | (5, 6) 22.3. | [17] |
| | $CDCl_3$ | (5, 6) 18.9 | [51] |
| 1-$CF_3$ 2,4-$H_2$ | | ($F_3C$, 2) 1, (3, 5) 11.3, (4, 5) 11.3, (5, $CF_3$) 1, (5, 6) 22.7, (6, $CF_3$) 7.1 | [19] |
| 1,5-$(CF_3)_2$ 2,4-$H_2$ | | (2, 3) 5.0, (6, $CF_3$) 8.0 | [57] |
| 1-$CHF_2$ 2,4-$H_2$ | | ($F_2CH$) 54.1 | [16] |
| 1-$CHF_2$ 2,5-$H_2$ | | ($F_2CH$) 54.1 | [16] |
| 1,4-$H_2$ 3-$NO_2$ | $CCl_4$ | (1, 2) 11, (1, 5) 1.5, (1, 6) 5, (2, 3) 22, (2, 4) 6.5, (2, 6) 11, (3, 5) 6, (3, 6) 5, (4, 5) 10, (4, 6) 2, (5, 6) 21.5 | [52] |

(*continued*)

Table 7 (*continued*)

| Substituent | Solvent | J, Hz | Ref. |
|---|---|---|---|
| 1,5,6-$H_3$ | $CDCl_3$ | (6F, 6H) 38.7 | [17] |
| 3-Cl 6,6-$(OMe)_2$ | | (*1, 3*) 7.0, (*2, 3*) 23.5 | [42] |
| 3-Cl 6,6-$(OEt)_2$ | | (*1,3*) 7.5, (*2,3*) 24.5 | [42] |
| 3-Cl 6,6-$(OPr^i)_2$ | | (*1, 3*) 6.5, (*2, 3*) 23.5 | [42] |
| 1,2,4,5-$H_4$ | hexane | (1, 3) 2.3, (2, 3) 2.3. | [54] |
| | hexane | (1, 3) 2.3, (2, 3) 2.3 | [23] |
| 1-$CHF_2$ 2,4,5-$H_3$ | | ($F_2CH$) 54.0 | [16] |
| 1,2,5-$H_3$ 6-Cl | | (3, 4) 19.8 | [55] |
| 1,4,5,6-$H_4$ | hexane | (2, 3A) 21.2, (2, 3B) 20.5, (2, 6) 1.7, (3A, 3B) 315.5, (3A, 6) 13.8, (3B, 6) 10.8, (6F, 6H) 43.3. | [23] |
| | $CDCl_3$ | (6F, 6H) 39.7 | [17] |
| 1-Cl 2,3,4,5-$H_4$ | | (3F, 3H) 42.2, (6A, 6B) 312 | [55] |
| 1,2,4,5,6-$H_5$ | hexane | (3A, 3B) 318.9, (3A, 6A) 15.3, (3A, 6B) 8.85, (3B, 4) 3.6, (3B, 6A) 11.3, (3B, 6B) 14.4, (6F, 6H) 43.5. | [23] |
| | $CDCl_3$ | (3F, 3H) 44.7, (6A, 6B) 320 | [26] |
| 1-$CF_3$ 2,3,4,5,-$H_4$ | $CDCl_3$ | (3A,3B) 325, (6F,6H) 42.2 | [26] |
| 1,3-$(CF_3)_2$ 2,4,5-$H_3$ | | (6A, 6B) 341 | [57] |
| 1,2,4,5-$H_4$ 3-$C_6H_5$ | $CCl_4$ | (6A, 6B) 310 | [58] |

[a]Perfluoro-1,4-cyclohexadien-1-yl.
[b]At 45°C.
[c]At −30°C.
[d]Apparent constant.
n.d.—not determined.
*—assignment was not done.
(?)—doubtful assignment.
*−123.5*—assignment assumed here.
1.23 (H)—$^1$H NMR chemical shift.
The blank space in the column 'Solvent' means absence of information about solvent in the original paper.

$$\delta(CF_2) = -(M + d + e) \quad (7)$$

$$\delta(CY) = -(N + d + e) \quad (8)$$

When they belong to the same C=C bond, Eqs. (9) and (10) were used.

$$\delta(CF_2) = -(M + 2d + e) \quad (9)$$

$$\delta(CY) = -(N + 2d + e) \quad (10)$$

| | | |
|---|---|---|
| Y=FF | $M=N=112.6$ | |
| Y=FCl | $M=110.8$ | $N=116.7$ |
| Y=$FNO_2$ | $M=111.8$ | $N=135.4$ |
| Y=FH | $M=108.5$ | $N=115.5$ |
| Y=O | $M=115.5$ | |

Table 8
Increments of substituents R (in ppm)

| R | Increments | | | | |
|---|---|---|---|---|---|
| | *a* (F-2) | *b* (F-4) | *c* (F-5) | *d* (F-3) | *e* (F-6) |
| H | −29.5 | 2.2 | −2.6 | 2.2 | −10.8 |
| Cl | −29.4 | 0.6 | −4.4 | −1.4 | −8.4 |
| Br | −37.1 | 1.3 | −4.9 | 0.0 | −10.3 |
| I | −51.9 | 1.6 | −6.6 | −0.5 | −16.7 |
| $CH_3$ | −20.4 | 3.3 | −1.5 | 1.3 | −4.5 |
| $CH_2F$ | −29.2 | 1.9 | −2.9 | 1.6 | −6.5 |
| $CHF_2$ | −33.1 | 2.6 | −2.4 | 1.6 | −8.4 |
| $CF_3$ | −41.0 | 1.6 | −4.0 | 1.1 | −8.1 |
| $C_6H_5$ | −24.4 | 2.8 | −3.1 | −0.6 | −10.1 |
| $C_6F_5$ | −35.8 | 1.1 | −4.3 | 1.0 | −8.5 |
| $OCHF_2$ | −10.7 | 1.2 | −0.9 | −0.1 | −2.5 |
| $NO_2$ | −37.3 | 0.7 | −3.5 | 0.2 | −6.0 |
| $SiMe_3$ | −41.2 | 3.8 | −4.5 | 1.2 | −15.4 |

Coefficients *M* and *N* are the δ (F) values of the geminal $CF_2$ and CY (Y = FF, FCl, $FNO_2$, FH) moieties in the $^{19}F$ NMR spectra of 3-Y-heptafluoro-1,4-cyclohexadienes and hexafluoro-1,4-cyclohexadien-3-one (Y = O) [59]. For Y = FH the values *M* and *N* were found from the spectrum of 1,6-diH-hexafluoro-1,4-cyclohexadiene using the increments *d* and *e* of hydrogen atom. For simplification the average chemical shift of the fluorine resonance F-6,6 in 3-X-3,6,6-tetrafluoro-1,4-cyclohexadienes was determined instead of those of the actual AB-signals. The corresponding values *M* and *N* for decafluorocyclohexene (Y = FF) (V.V. Bardin, unpublished results) and octafluorocyclohexen-3-one (Y = O) [60] can be taken from original papers.

The accuracy of the predicted chemical shifts of the allylic fluorines $\Delta\delta\ (F) = (\delta_{calc} - \delta_{exp})$ was confirmed by examination: (1) Δδ (F) ≤ 1–2 ppm (X = F, Cl, $NO_2$) and Δδ (F) ≤ 2–3 ppm (X = H) for fluorinated 1,4-cyclohexadienes (for all data presented in Tables 3–5), (2) Δδ (F) ≤ 1.5 ppm for 1-R- and 2-R-pentafluoro-1,4-cyclohexadien-3-ones (R = H, Cl, Br, $CH_3$, $CF_3$, $C_6F_5$, $OCHF_2$) and 1,2,4,5-tetrachloro-6,6-difluoro-1,4-cyclohexadien-3-one, (3) Δδ (F) ≤ 1.5 ppm for 1-R-nonafluorocyclohexenes (all R listed in Table 8 except $NO_2$) and 1-$R^1$-2-$R^2$-octafluorocyclohexenes ($R^1$ = H, $R^2$ = H, Cl, Br, $CHF_2$, $CF_3$, $NO_2$; $R^1$ = Cl, $R^2$ = $SiMe_3$, $CH_3$; $R^1$ = $C_6F_5$, $R^2$ = $C_6H_5$; $R^1$ = $R^2$ = Cl, $CF_3$). (4) Δδ (F) ≤ 2.5 ppm for 1-$R^1$-2-$R^2$-heptafluorocyclohexen-3-ones ($R^1$ = Cl, $R^2$ = F; $R^1$ = Br, $R^2$ = F; $R^1$ = F, $R^2$ = Cl; $R^1$ = $R^2$ = Cl).

In a few cases the error Δδ (F) were found to be up to 4 to 4.5 ppm.

## 3. Conclusion

The good coincidence between $\delta\ (F)_{exp}$ and $\delta\ (F)_{calc}$ values for fluorinated 1,4-cyclohexadienes, 1,4-cyclohexadien-3-ones, cyclohexenes and cyclohexen-3-ones shows the common character of the substituent increments presented in Table 8 in these series. The errors Δδ (F) do not exceed 1.5 and 2.5 ppm for vinylic and allylic fluorine atoms, respectively. In a few cases they increased to 2–4 ppm and there are some possible reasons for these deviations: (a) experimental (temperature- and solvent-dependence of fluorine chemical shifts, influence of admixtures, technical errors in measurements), (b) conformational differences of the analysed molecule from its perfluorinated formal precursor and (c) specific interaction of substituents which is not displayed in the simple models. However, the offered estimation of δ (F) values is a convenient tool for the primary identification of six-membered fluorocycloalkenes and for the assignment of the resonances in their $^{19}F$ NMR spectra if the analysis of the spin–spin coupling constants is impossible or ambiguous. This approach can be also used for determination of the other substituent increments which are not included in Table 8.

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