The ^{13}C NMR of Monochlorocarbazoles, Monochlorotetrahydrocarbazoles and Their 9-Methyl Derivatives [1]

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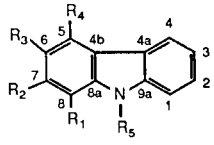
Received December 3, 1986

The ^{13}C nmr of monochlorocarbazoles, monochlorotetrahydrocarbazoles and their 9-methyl derivatives were measured and the chlorine effects at the *ipso, ortho, meta,* and *para* carbons determined.

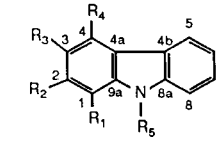
J. Heterocyclic Chem., **25**, 167 (1988).

Carbazole and its derivatives have been the subject of various ^{13}C nmr studies [2-11]. Several of these have looked at the transmission of substituent effects in the carbazole series [7b,8]. This study reports on the ^{13}C nmr of monochlorocarbazoles and their 9-methyl derivatives. In this manner it is possible to examine the effect of chlorine substitution at different positions on the carbon resonances of carbazole. A study of this type has not been previously carried out in the carbazole system. Chlorocarbazoles [12,13] were prepared from the corresponding tetrahydrocarbazoles [12] and their spectra are also reported. The ^{13}C nmr spectra of the following are reported.

Scheme 1



1, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
2, $R_1 = R_2 = R_3 = R_4$, $R_5 = CH_3$
3, $R_2 = R_3 = R_4 = R_5 = H$, $R_1 = Cl$
4, $R_2 = R_3 = R_4 = H$, $R_1 = Cl$, $R_5 = CH_3$
5, $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = Cl$
6, $R_1 = R_3 = R_4 = H$, $R_2 = Cl$, $R_5 = CH_3$
7, $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = Cl$
8, $R_1 = R_2 = R_4 = H$, $R_3 = Cl$, $R_5 = CH_3$
9, $R_1 = R_2 = R_3 = R_5 = H$, $R_4 = Cl$
10, $R_1 = R_2 = R_3 = H$, $R_4 = Cl$, $R_5 = CH_3$



11, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
12, $R_1 = R_2 = R_3 = R_4$, $R_5 = CH_3$
13, $R_2 = R_3 = R_4 = R_5 = H$, $R_1 = Cl$
14, $R_2 = R_3 = R_4 = H$, $R_1 = Cl$, $R_5 = CH_3$
15, $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = Cl$
16, $R_1 = R_3 = R_4 = H$, $R_2 = Cl$, $R_5 = CH_3$
17, $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = Cl$
18, $R_1 = R_2 = R_4 = H$, $R_3 = Cl$, $R_5 = CH_3$
19, $R_1 = R_2 = R_3 = R_5 = H$, $R_4 = Cl$
20, $R_1 = R_2 = R_3 = H$, $R_4 = Cl$, $R_5 = CH_3$

Assignment of Carbon Resonances.

Substituent effects in the carbazole series often have been calculated from a simple monosubstituted benzene [10]. In this study the assignment of the carbons of the monochlorotetrahydrocarbazole was first carried out with the aid of proton coupled spectra and, where possible, selective single proton decoupling. Carbazole assignments then were checked by comparing the assigned values with those calculated by adding the effect of aromatizing tetrahydrocarbazole (**1**) to carbazole (**11**) or **2** to **12** (Table 1) to the carbons of the monochlorotetrahydrocarbazole.

Table 1

Effect of Aromatization on ^{13}C Resonances of Tetrahydrocarbazole and 9-Methyltetrahydrocarbazole [a]

C	**1**	**2**	**11**	**12**	**1→11**	**2→12**
1	23.3	21.8	110.7	108.2	87.4	86.4
2	23.2	23.2	125.3	125.9	102.1	102.7
3	23.2	23.2	118.6	118.7	95.4	95.5
4	20.9	21.0	119.9	120.1	99.0	99.1
4a	109.9	108.7	122.9	122.6	13.0	13.9
4b	127.6	127.0	122.9	122.6	−4.7	−4.4
5	117.5	117.4	119.9	120.1	2.4	2.7
6	118.9	118.2	118.6	118.7	−0.3	0.5
7	120.8	120.1	125.3	125.9	4.5	5.8
8	110.2	108.2	110.7	108.2	0.5	0.0
8a	135.5	136.5	139.7	140.8	4.2	4.3
9a	133.9	135.2	139.7	140.8	5.8	5.6
CH_3	— — —	28.4	— — —	29.0	— — —	0.6

[a] Deuteriochloroform and TMS as internal reference. Values are ± 0.2 ppm.

A ^{13}C nmr spectrum of tetrahydrocarbazole (**1**), in deuteriochloroform and using carbon disulfide as an external reference, has been reported [14]. These values were recalculated for TMS as the internal standard and agree with those reported here (Table 1). Carbons 1-4 of **1** have not been previously assigned. Selective proton decoupling was used to distinguish C-1/C-4 (2.63 ppm) from C-2/C-3 (1.87 ppm). Values in parentheses are the chemical shifts of the

proton(s) decoupled. In all the tetrahydrocarbazoles studied, the carbon of the C-1/C-4 pair which appeared at lower field was assigned to C-1. This gave consistent results when calculating the carbon resonances of the chlorocarbazoles.

Single proton decoupling was used to assign the carbon resonances of the protonated carbons of 6-chlorotetrahydrocarbazole (**7**) C-1/C-4 (2.68 ppm), C-2/C-3 (1.88 ppm), C-5 (7.40 ppm), C-7 (7.00 ppm), and C-8 (7.16 ppm). Quaternary carbons were assigned by analogy with **1**. The protonated and quaternary carbons of 7-chlorotetrahydrocarbazole (**5**) were similarly assigned: C-1/C-4 (2.50 ppm), C-2/C-3 (2.00 ppm), C-5 (7.34 ppm), C-6 (7.03 ppm), and C-8 (7.24 ppm).

The aromatic peaks of the ^{1}H nmr spectra of 8-chlorotetrahydrocarbazole (**3**) and 5-chlorotetrahydrocarbazole (**9**) were not sufficiently resolved to carry out selective proton decoupling. Their carbon resonances were assigned by comparison with those of **1**, **5** and **7**. Spectra of the 9-methyltetrahydrocarbazoles were assigned by comparison with the unmethylated products. Table 2 summarizes the ^{13}C nmr data for the chlorotetrahydrocarbazoles **3-10**.

Table 3 summarizes the experimental and calculated carbon resonances of chlorocarbazoles **13-20**. Proton coupled ^{13}C nmr spectra were taken of 1-chlorocarbazole (**13**) and 4-chlorocarbazole (**19**) and confirmed the assignments calculated for **13** and **19**. Values calculated for carbazoles **13-18** (Table 4), using aromatization effects, generally agreed well with experimental values (± 1 ppm) except for several carbons in the 1-chloro and 3-chloro derivatives. There existed significant deviations between the experimental and calculated spectra of 4-chlorocarbazole (**19**) and 9-methyl-4-chlorocarbazole (**20**). A calculation [15], based on crystalographic data (carbazole [16]) and the appropriate bond lengths [17] and Van der Waals radii [18], indicated a small steric interaction between the chlorine at C-4 and C-5H. Similar results were obtained using the Molecular Editor® program [19]. This interaction is similar to that observed in the electronic spectra [20] and reactions [21] of 4,5-dimethylcarbazoles. The deviations between the calculated and experimental values for **19** and **20** are attributed to this steric interaction. A steric interaction can also be seen in the analogous chlorotetrahydrocarbazole. Carbon 4 in chlorotetrahydrocarbazoles **3**, **5**, and **7** (Table 5) was effected slightly (± 0.2 ppm); but in 5-chlorotetrahydrocarbazole (**9**) C-4 was shifted + 1.6 ppm. This change is incompatible with an inductive effect.

The ^{13}C nmr spectrum of 3-chloro-9-methylcarbazole (**18**) has been previously reported [8a] and the assignments for C-4/C-5 and C-8a/C-9a are interchanged with respect to those reported here. Only a slight difference (0.6 ppm) exists between C-4 and C-5 but the difference between C-8a and C-9a is greater (2.1 ppm).

Discussion.

Substituent effects on ^{13}C resonances of aromatic compounds are generally considered to be additive [22]. Experimental and calculated values are generally in good agreement (± 1 ppm) when steric interactions are not present. The results in Table 4 indicate that the method used for calculating the ^{13}C shifts of chlorocarbazoles fits this criterion.

Chlorine substituent effects on the ^{13}C chemical shifts of benzene [23] and polycyclic aromatic compounds [24-26]

Table 2

^{13}C NMR Spectra of Chlorotetrahydrocarbazoles [a]

C	3	4	5	6	7	8	9	10
1	23.3	22.3	23.2	21.7	23.2	22.1	23.3	22.2 [c]
2	23.3	23.4 [b]	23.2 [b]	22.8	23.2	23.3 [b]	23.0 [b]	23.4 [b]
3	23.3	23.2 [b]	23.1 [b]	22.8	23.1	23.9 [b]	22.8 [b]	23.0 [b]
4	21.1	21.1	20.8	20.7	20.8	21.1	22.5	22.7 [c]
4a	111.5	110.1	110.6	109.4	110.3	109.5	109.7	109.6
4b	129.7	130.7	127.0 [c]	126.4	129.4	128.7	125.2	125.8
5	116.4	116.4	118.8	118.3	117.6	117.2	124.8	124.6
6	119.9	119.3	119.9	118.9	125.0	124.4	119.3	119.3
7	120.4	122.4	126.9 [c]	125.8	121.3	120.4	121.0	120.7
8	116.0	116.4	110.6	108.4	111.5	109.4	109.0	106.9
8a	135.0	137.4	136.4	137.1	136.1	137.4	136.5	138.2
9a	133.2	132.5	135.2	136.5	134.4	135.6	135.1	136.5
CH_3	– – –	31.5	– – –	28.6	– – –	28.8	– – –	29.6

[a] Deuteriochloroform and TMS as internal standard. Values are ± 0.2 ppm. [b,c] Interchangeable.

Table 3

^{13}C NMR of Chlorocarbazoles [a]

C	13	14	15	16	17	18	19	20
1	116.0	116.1	112.0 [c]	108.5	111.4	109.0	109.4	106.7
	(116.5) [b]	(116.4)	(111.9)	(108.4)	(112.0)	(109.4)	(109.5)	(106.9)
2	124.9	126.3	131.8	131.4	126.4	125.2	127.0	126.4
	(124.9)	(128.2)	(132.3)	(131.6)	(125.8)	(126.2)	(125.5)	(126.5)
3	120.0	119.5	120.3	119.2	124.4	123.4	120.7	119.9
	(119.6)	(119.8)	(120.8)	(119.4)	(124.7)	(124.9)	(119.0)	(119.8)
4	120.5	120.1	122.0	120.9	120.3	119.5	129.4	128.9
	(118.8)	(119.1)	(121.9)	(121.0)	(120.0)	(119.9)	(127.2)	(127.3)
4a	124.9	126.3	123.0	121.3	124.8	123.9	121.2	120.2
	(125.0)	(126.3)	(123.4)	(122.0)	(124.7)	(124.3)	(120.5)	(121.4)
4b	123.6	122.5	123.6	122.2	122.4	121.4	122.9	122.1
	(124.5)	(124.0)	(124.7)	(123.3)	(123.3)	(123.4)	(122.7)	(123.5)
5	120.0	119.5	121.0	120.1	119.9 [d]	120.1	123.8	123.5
	(120.1)	(120.2)	(120.5)	(119.8)	(119.8)	(120.2)	(121.5)	(121.8)
6	118.5	118.6	120.1	119.2	119.6 [d]	118.8	120.3	119.6
	(118.7)	(118.7)	(119.7)	(118.3)	(118.5)	(119.4)	(118.2)	(118.5)
7	126.4	127.3	126.9	125.8	125.7	126.0	126.6	125.9
	(125.4)	(126.1)	(126.2)	(125.5)	(125.3)	(126.0)	(125.1)	(126.1)
8	110.9	108.7	111.7	108.5	110.6	108.3	110.9	108.3
	(110.7)	(108.7)	(111.4)	(108.1)	(110.6)	(108.5)	(110.7)	(108.6)
8a	139.4	142.0	141.8 [d]	141.4 [d]	139.8	140.9	141.4	142.3
	(139.0)	(138.1)	(141.9)	(142.1)	(140.2)	(141.2)	(140.9)	(142.1)
9a	136.8	142.0	141.6 [d]	141.1 [d]	137.6	138.8	140.4	141.2
	(139.2)	(141.7)	(141.5)	(141.4)	(140.3)	(141.7)	(140.7)	(142.5)
CH_3	– – –	31.7	– – –	29.7	– – –	28.7	– – –	29.8
	– – –	(32.1)	– – –	(29.2)	– – –	(29.4)	– – –	(30.2)

[a] Deuteriochloroform and TMS as internal standard. Values are ± 0.2 ppm. [b] Values in parenthesis have been calculated by adding the appropriate factor from Table 1 to the carbon resonance of the analogous chlorotetrahydrocarbazole (Table 2). [c] Perdeuterioacetone. Corrected for solvent effect on 11: C-1 (+0.8), C-2 (+0.9), C-3 (+1.2), C-4 (+0.7), C-4a (+1.1) and C-8a (+0.9). [d] Interchangeable.

Table 4

Difference between Experimental and Calculated ^{13}C NMR Spectra of Chlorocarbazoles [a]

C	13	14	15	16	17	18	19	20
1	−0.5	−0.3	+0.1	+0.1	−0.6	−0.4	−0.1	−0.2
2	0.0	−1.9	−0.5	−0.2	+0.6	−0.1	+1.5	−0.1
3	+0.4	−0.3	−0.5	−0.2	−0.3	−1.5	+1.7	+0.1
4	+1.7	+1.0	+0.1	−0.1	+0.3	−0.4	+2.2	+1.6
4a	−0.1	0.0	−0.4	−0.7	+0.1	−0.4	+0.7	−1.2
4b	−0.9	+1.5	−1.1	−1.1	−0.9	−2.0	+0.2	−1.4
5	−0.1	−0.7	+0.5	+0.3	+0.1	−0.1	+2.3	+1.4
6	−0.2	−0.1	+0.4	+1.1	+1.1	−0.6	+2.1	+1.1
7	+1.0	+1.2	+0.7	+0.3	+0.4	0.0	+1.5	−0.2
8	+0.2	0.0	+0.3	+0.4	0.0	−0.2	+0.2	−0.3
8a	+0.4	+3.9	−0.1	−0.7	−0.4	−0.3	+0.5	+0.2
9a	−2.4	+0.3	+0.1	−0.3	−2.7	−2.9	−0.3	−1.3

[a] δ Experimental − δ Calculated.

have been reported. Similar effects [27] are noted at the carbons *ipso* (deshielded), *meta* (deshielded) and *para* (shielded) to the chlorine atom. *Ortho* positions are subject to steric interactions and substituent effects are variable. The effect of a chlorine atom on the carbons of the substituted ring in chlorotetrahydrocarbazoles and chlorocarbazoles can be seen in Table 5 and 6 respectively.

Chlorine effects at the *ipso*, *ortho* and *meta* carbons are similar to those observed in benzene and polycyclic aromatic compounds [27]. But the carbon *para* to the chlorine atom is not uniformly shielded in all the compounds studied. In 1-chloro- and 2-chlorocarbazole and also 6-chlorotetrahydrocarbazole, the *para* carbon experiences a deshielding effect. This would seem to imply that the inductive effect of the chloro group was stronger than its resonance effect in these compounds.

Examination of the ^{13}C chemical shifts of the 9-methyl group indicated, that apart from **4** and **14**, the chlorine atom had little effect on the chemical shift of the methyl

Table 5

Observed Chlorine Substituent Effects on Carbon Chemical Shifts of Chlorotetrahydrocarbazoles [a]

Compound	Substituted Ring				Unsubstituted Ring					
	Ipso	*Ortho*	*Meta*	*Para*	C-1	C-2	C-3	C-4	C-4a	C-9a
3	+5.8	−0.4 (C-7) −0.5 (C-8a)	+1.0 (C-6) +2.1 (C-4b)	−1.1	0.0	+0.1	+0.1	+0.2	+1.6	−0.5
5	+6.1	+1.0 (C-6) +0.4 (C-8)	+1.3 (C-5) +0.9 (C-8a)	−0.6	−0.1	0.0	−0.1	−0.1	+0.7	+1.3
7	+6.1	+0.1 (C-5) +0.5 (C-7)	+1.3 (C-8) +1.8 (C-4b)	+0.6	−0.1	0.0	−0.1	−0.1	+0.4	+0.5
9	+7.3	+0.4 (C-6) −2.4 (C-4b)	+0.2 (C-7) +1.0 (C-8a)	−1.2	0.0	−0.2	−0.4	+1.6	−0.2	+1.2

[a] Positive values indicate downfield shifts.

Table 6

Observed Chlorine Substituent Effects on Carbon Chemical Shifts of the Substituted Ring of Chlorocarbazoles [a]

Substituent	*Ipso*	*Ortho*	*Meta*	*Para*
1-Cl	+5.3	−0.4 (C-2) −2.9 (C-9a)	+1.4 (C-3) +2.0 (C-4a)	+0.6
2-Cl	+6.5	+1.3 (C-1) +1.7 (C-3)	+2.1 (C-4) +1.9 (C-9a)	+0.1
3-Cl	+5.8	+1.1 (C-2) +0.4 (C-4)	+0.7 (C-1) +1.9 (C-4a)	−2.1
4-Cl	+9.5	+2.1 (C-3) −1.7 (C-4a)	−1.7 (C-2) +0.7 (C-9a)	−1.3

[a] Positive values indicate downfield shifts.

group. A steric interaction between the chloro and methyl group was the most likely cause of the larger chemical shifts noted in **4** and **14**.

EXPERIMENTAL

The preparation [12-13] and ^{1}H nmr spectra [13] of the monochlorocarbazoles, monochlorotetrahydrocarbazoles and their 9-methyl derivatives have been previously described.

The ^{13}C nmr spectra were obtained at 25.2 MHz on a Varian XL-100 FT NMR spectrometer using a 6201-100 computer interfaced to a Diablo 33 disk drive. Spectra were taken of 0.25 g samples dissolved in 2.5 ml of deuteriochloroform containing TMS as the internal standard in a 12 mm tube at *ca* 37° at a spectral width of 5000 Hz using 14 μsec pulses, an acquisition time of 1.6 sec and a pulse delay of 0.6 sec. An 8K data table was used giving a digital resolution (data length) of 1.25 Hz per point. Totally decoupled spectra are the results of 1000 pulses and were obtained by hetero noise decoupling at high power (10 W) with a band width of 2000 Hz set at 0 ppm. Selectively decoupled spectra were obtained by homonuclear decoupling at low power.

Some spectra were taken with a Varian FT-80A (Universidad de los Andes) under similar conditions.

Acknowledgement.

We thank Ing. J. Serra (Universidad Simón Bolívar) and Dr. Uzubillaga (Universidad de los Andes) for the ^{13}C nmr spectra.

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