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^1H and ^{13}C NMR spectra of several substituted carbazoles (Series 1, 2, 3, 4 and 5) were measured. Substituent chemical shifts (SCS's) and Lynch correlations of ^1H and ^{13}C nuclei were calculated and the substituent effect on the NMR phenomena was determined. Atomic charge densities for carbazoles of Series 1, 2, 3, 4 and 5 were calculated by using the semi empirical PM3 method. These values also show a linear correlation with the ^{13}C chemical shifts.

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Introduction.

Nuclear magnetic resonance parameters, mainly chemical shifts, have been widely applied as a probe of electronic substituent effects [1-5]. The utility of this technique is based on the linear dependence between the measured substituent induced chemical shifts (SCSs) and the calculated electron densities. To determine the extent of transmission of these effects in aromatic derivatives, ^{13}C is the most frequently used nuclei [1]. In our previous publication [6], we analysed the substituent effect on the ^{13}C NMR chemical shifts of mono substituted carbazoles. According to our knowledge carbazole and its derivatives have been the subject of various ^{13}C NMR studies [6-7]. Several of these have looked at the transmission of the substituent effects in the carbazole series (some *N*-alkyl carbazoles and *C*-substituted *N*-methylcarbazoles) [6]. De Rosa *et al.* [8] have analyzed the chlorine atom effect on ^{13}C NMR chemical shifts of monochlorocarbazole derivatives. However, no detailed substituent chemical shift analyses were performed on more functionalised carbazole derivatives.

This study reports the ^1H and ^{13}C NMR chemical shifts of several mono, di and poly substituted carbazoles (Series 1 – 5) shown in Scheme I with a view to understanding the factors underlying the transmission of substituent effects in these systems. Also, we correlate the ^{13}C chemical shifts of carbons at *ipso*, *ortho*, *meta* and *para* position and the net atomic charge densities on the same carbon atoms in carbazoles of Series 1 - 5 and the dependence of these quantities are analysed. The numbering system of carbazole and its derivatives used for the present work is shown in Figure 1.

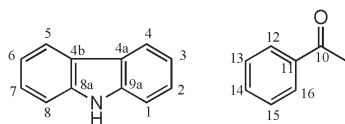


Figure 1. Atomic Numbering of Carbazoles.

Results and Discussion.

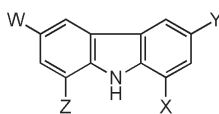
Correlation of ^1H NMR Chemical Shifts.

Assignments of the ^1H and ^{13}C chemical shifts were based on consideration of peak intensity, peak multiplicity under off-resonance ^1H decoupling and with complete ^1H coupling. All assignments were verified by 2D NMR spectroscopy. Table I lists the proton chemical shifts of carbazole and its derivatives (Series 1-5, see Scheme I), accurate to 0.02 ppm. Table II shows the ^1H NMR substituent chemical shifts for carbazoles in Series 1-5. The ^1H chemical shifts for Series 1-5 were assigned with very few ambiguities. A wide singlet is usually present for NH of compounds in Series 1-5 in the range of 9.00 to 11.5 ppm, depending on the substituents attached to the carbazole moiety. The ^1H signals appearing downfield in the range of 7.70 – 8.60 ppm were assigned to 4-H and 5-H in view of the known deshielding at *peri*-positions for compounds in Series 1-5.

The effect of the chlorine substituent at the *ortho*-positions (2-H, 4-H, 5-H and 7-H) shows negative values that indicate a uniformly upfield shift (see Table II). In chlorocarbazoles 2-6, the *ortho*-hydrogens experience a shielding effect. This would seem to imply that the resonance effect of the chlorine group was stronger than its inductive effect in these compounds. It is noteworthy to mention that in 1, 3, 6, 8-tetrachlorocarbazole, the *ortho*-hydrogen atoms (2-H, 4-H, 5-H and 7-H) show a moderate deshielding effect (downfield shift). It could be concluded that the presence of four chlorine atoms in the carbazole moiety enhance the inductive effect over the resonance effect at the *ortho*-hydrogen atoms taking into account the electronegativity of the chlorine atoms.

The substituent effect at the *ortho*-position (2-H, 4-H, 5-H and 7-H) of bromo, iodo, benzoyl and nitro carbazole derivatives (Series 2, 3, 4 and 5) show a deshielding effect (downfield shift) as it is expected when these kind of substituents are attached to the carbazole moiety (see Table II). This behaviour implies that the inductive effect of the bromo or iodo group is stronger than its resonance effect

Scheme I. Structure of the carbazoles studied.



Compd.	Series 1				Compd.	Series 2				Compd.	Series 3			
	X	Y	W	Z		X	Y	W	Z		X	Y	W	Z
1	H	H	H	H	8	Br	H	H	H	13	I	H	H	H
2	Cl	H	H	H	9	H	Br	H	H	14	H	I	H	H
3	H	Cl	H	H	10	H	Br	Br	H	15	I	H	I	H
4	Cl	H	Cl	H	11	Br	Br	Br	H	16	H	I	I	H
5	H	Cl	Cl	H	12	Br	Br	Br	Br	17	I	I	I	H
6	Cl	Cl	Cl	H										
7	Cl	Cl	Cl	Cl										

Compd.	Series 4				Compd.	Series 5			
	X	Y	W	Z		X	Y	W	Z
18	COPh	H	H	H	21	NO ₂	H	H	H
19	H	COPh	H	H	22	NO	NO ₂	H	H
20	H	COPh	COPh	H	23	NO ₂	H	NO ₂	H
					24	H	NO ₂	NO ₂	H

Table I

¹H Chemical Shifts of polysubstituted carbazoles [a]

Protons	Compounds											
	1	2	3	4	5	6	7	8	9	10	11	12
1-H	7.16	-	7.05	-	7.33	-	-	-	7.40	7.50	-	-
2-H	7.48	7.42	7.36	7.43	7.38	7.45	7.50	7.50	7.50	7.55	7.77	7.70
3-H	7.36	7.20	-	7.21	-	-	-	7.40	-	-	-	-
4-H	8.10	7.95	7.95	7.95	7.96	7.70	8.17	7.99	8.34	8.30	8.26	8.44
5-H		8.04	7.85	7.94		7.81		8.06	8.09		8.27	
6-H		7.58	7.60	-		-		7.52	7.61		-	
7-H		7.42	7.42	7.40		7.41		7.42	7.43		7.54	
8-H		7.20	7.19	7.15		7.35		7.16	7.16		7.50	
Protons	13	14	15	16	17	18 [b]	19 [b]	20 [b]	21	22	23	24
1-H	-	7.37	-	7.36	-	-	7.54	7.58	-	7.65	-	7.75
2-H	7.77	7.65	7.80	7.67	8.02	8.17	8.10	8.05	8.24	8.29	8.39	8.38
3-H	6.98	-	6.99	-	-	7.52	-	-	7.35	-	7.49	-
4-H	8.13	8.51	8.18	8.57	8.57	8.36	8.54	8.58	8.62	9.15	8.90	9.45
5-H	8.09	8.15	8.50		8.55	8.11	7.92		8.31	8.36	9.30	
6-H	7.20	7.18	-		-	7.40	7.42		7.29	7.51	-	
7-H	7.43	7.43	7.69		7.70	7.38	7.39		7.51	7.29	8.50	
8-H	7.61	7.52	7.45		7.43	7.18	7.20		8.41	7.58	7.88	

[a] Values in parts per million (ppm). Internal reference: tetramethylsilane. [b] Other protons. Compound **18**: 7.83 (11-H and 15-H); 7.52 (12-H and 14-H); 7.30 (13-H); Compound **19**: 7.86 (11-H and 15-H); 7.54 (12-H and 14-H); 7.30 (13-H); Compound **20**: 7.86 (11-H and 15-H); 7.53 (12-H and 14-H); 7.32 (13-H).

while, in the cases of benzoyl and nitro groups, the withdrawing resonance effect (*-R*) accounts for the deshielding effect on the hydrogen chemical shifts.

The substituent effect at the *meta*-positions of carbazoles in Series 1-5 shows a downfield shift (deshielding effect).

Table II shows the substituent effect at *para*-position (4-H) for carbazoles in Series 1-5. When chlorine and bromine atoms are attached to the carbazole moiety a substituent chemical shift with negative values are obtained. This

implies that a shielding effect (upfield shift) operates. This behaviour could be ascribed to an important inductive effect which is transmitted through the carbon nuclei. When the substituent group is an iodine atom, a small downfield shift is observed and could be ascribed to van der Waals deshielding and/or anisotropic effects. Likewise, when the benzoyl and nitro groups are attached to the carbazole moiety, a positive substituent chemical shift value is observed due to a moderate deshielding effect (downfield shift). This

Table II
 ^1H Substituent chemical shift of polysubstituted carbazoles [a]

Compd.	<i>ortho</i>	<i>meta</i>	<i>para</i>
2	-0.06 (2-H)	-0.16 (3-H)	-0.15 (4-H)
3	-0.12 (2-H); -0.15 (4-H)	-0.11 (1-H)	-
4	-0.13 (2-H); -0.15 (5-H); -0.13 (7-H)	-0.01 (3-H); -0.04 (8-H)	-0.15 (4-H)
5	-0.10 (2-H); -0.14 (4-H)	0.17 (1-H)	-
8	0.02 (2-H)	0.04 (3-H)	-0.11 (4-H)
9	0.02 (2-H); 0.24 (4-H)	0.24 (1-H)	-
10	0.07 (2-H); 0.20 (4-H)	0.34 (1-H)	-
13	0.29 (2-H)	-0.38 (3-H)	0.03 (4-H)
14	0.17 (2-H); 0.41 (4-H)	0.21 (1-H)	-
15	0.32 (2-H); 0.40 (5-H); 0.21 (7-H)	-0.37 (3-H); 0.29 (8-H)	0.08 (4-H)
16	0.19 (2-H); 0.47 (4-H)	0.20 (1-H)	-
18	0.69 (2-H)	0.16 (3-H)	0.26 (4-H)
19	0.62 (2-H); -0.56 (4-H)	0.38 (1-H)	-
20	0.27 (2-H); 0.48 (4-H)	0.42 (1-H)	-
21	0.76 (2-H)	0.01 (3-H)	0.52 (4-H)
22	0.81 (2-H); 1.05 (4-H)	0.49 (1-H)	-
23	0.91 (2-H); 1.20 (5-H); 0.89 (7-H)	0.13 (3-H); 0.72 (8-H)	0.80 (4-H)
24	0.90 (2-H); 1.35 (4-H)	0.59 (1-H)	-

[a] Positive values indicate downfield shifts.

trend implies that the resonance effects of the benzoyl and nitro groups are stronger than their inductive effect.

Similar results and trends of the ^1H NMR chemical shifts produced by the same family of substituents (Cl, Br, I, C₆H₅ and NO₂) were observed in polycyclic hydrocarbons (naphthalene [9]; acenaphthenes [10]).

The substituent chemical shift at 4-H of tri- and tetra-substituted carbazoles in Series 1-3 (see Scheme I) shows an enhancement in their values; SCS value of compound **6** amounts to -0.40 ppm, for compound **17** the SCS value is +0.47 ppm, for compound **7** the SCS value is +0.07 ppm and compound **12** shows a SCS value of +0.34 ppm. These values mean that the substituent chemical shift is additive taking into account that in these compounds, for example, the 4-H is, at the same time, in *ortho*- and *para*-positions with respect to the substituents attached to the

carbazole moiety. Thus, the *ortho* and the *para* effects of the substituents operate simultaneously.

We also performed the Lynch correlations in order to estimate quantitatively the influence of the substituent chemical shift of *ortho*-hydrogen atoms (2-H, 4-H, 5-H and 7-H) and *para*-hydrogen (4-H) of carbazoles in Series 1-5. The Lynch correlations afford good linear plots even though few numbers of substituent groups (Cl, Br, I, C₆H₅ and NO₂) are used for this analysis and the results are shown in Table III. The slope values for the *ortho*- and *para*-hydrogen atoms are greater than 1.00 suggesting that the chemical shifts are influenced more significantly in the carbazole moiety than in monosubstituted benzenes.

The substituent chemical shift on *meta*-hydrogen atoms (1-H, 3-H and 8-H) does not afford reasonable Lynch correlations due to a large spread of the data (scattered plot).

Table III
 Lynch correlations of ^1H chemical shifts of substituted carbazoles.

	1-substituted carbazoles		3-substituted carbazoles			Ortho-hydrogens 1,6-disubstituted carbazoles			3,6-disubstituted carbazoles	
	2-H		2-H	4-H	2-H	5-H	7-H	2-H	4-H	
Slope	0.99		1.08	1.19	1.14	1.23	1.12	1.12	1.21	
r ²	0.985		0.959	0.967	0.998	0.997	0.992	0.975	0.978	
Para-hydrogens										
1-Substituted carbazoles										
1,6-Disubstituted carbazoles										
4-H										
4-H										
Slope			1.39		1.98					
r ²			0.986		0.997					

Table IV
 ^{13}C Chemical Shift of polysubstituted carbazoles [a]

Carbons	Compounds											
	1	2	3	4	5	6	7	8	9	10	11	12
1-C	110.8	116.5	113.0	112.3	112.5	116.0	116.8	102.5	112.8	112.9	105.2	105.1
2-C	125.3	126.5	126.2	126.3	125.9	126.9	126.0	127.8	127.8	128.5	131.1	131.5
3-C	118.4	120.2	123.4	119.7	123.0	123.2	124.0	120.6	110.8	110.8	112.2	111.9
4-C	119.5	118.7	120.4	188.8	120.1	119.4	119.5	118.9	122.6	123.1	123.3	123.1
5-C	-	120.8	119.8	120.6	-	120.7	-	122.4	120.6	-	124.4	-
6-C	-	120.0	117.8	123.7	-	120.7	-	119.6	118.9	-	114.3	-
7-C	-	125.1	125.6	125.3	-	124.9	-	126.2	126.2	-	130.5	-
8-C	-	111.0	110.7	111.2	-	113.2	-	111.1	111.1	-	113.2	-
4a-C	122.4	122.4	122.8	122.9	122.6	124.1	124.1	124.3	124.4	123.4	123.9	124.4
4b-C	-	125.0	122.9	121.6	-	124.0	-	122.4	121.4	-	122.0	-
9a-C	139.4	140.3	138.9	140.4	138.5	135.8	136.1	139.6	138.4	138.6	139.5	138.6
8a-C	-	139.3	139.4	138.2	-	138.9	-	138.2	140.1	-	140.1	-

Carbons	Compounds											
	13	14	15	16	17	18 [b]	19 [b]	20 [b]	21	22	23	24
1-C	72.5	113.3	73	113.5	77.9	120.1	111.8	110.6	140.6	111.7	132.4	112.4
2-C	134.0	133.3	134.8	134.0	140.9	125.6	129.6	127.9	121.6	121.1	119.9	122.7
3-C	120.0	81.2	120.8	81.7	82.0	119.3	128.5	130.0	127.9	143.1	123.2	149.8
4-C	120.4	128.6	120.5	129.1	128.9	126.5	120.9	123.9	132.8	116.9	129.2	128.8
5-C	120.6	120.5	129.1	-	129.6	117.5	120.3	-	120.5	120.9	116.5	-
6-C	119.2	118.9	82.2	-	82.7	118.3	118.2	-	118.2	120.0	140.0	-
7-C	126.1	126.2	134.0	-	134.7	125.8	124.6	-	127.1	127.3	122.6	-
8-C	111.7	111.0	114.1	-	114.2	110.3	111.0	-	112.6	110.9	112.9	-
4a-C	123.0	125.1	125.5	123.8	124.2	124.6	123.3	122.8	127.1	122.2	124.6	122.7
4b-C	122.6	121.1	121.7	-	123.8	122.1	123.7	-	121.4	121.9	121.4	-
9a-C	141.4	139.7	139.6	138.8	141.2	138.2	139.4	138.3	130.9	139.6	129.1	141.0
8a-C	139.5	138.7	138.6	-	138.7	143.0	141.2	-	131.6	140.8	132.1	-

[a] Values in part per million (ppm). Internal reference: tetramethylsilane. [b] Other carbon atoms. Compound **18**: 130.6 (10-C); 128.1 (11-C and 15-C); 197.4 (CO); 131.3 (13-C); 129.2 (12-C and 14-C); Compound **19**: 128.6 (10-C); 130.3 (11-C and 15-C); 198.4 (CO); 132.4 (13-C); 128.7 (12-C and 14-C); Compound **20**: 128.6 (10-C); 130.3 (11-C and 15-C); 198.4 (CO); 132.4 (13-C); 128.7 (12-C and 14-C).

Finally, in order to verify whether the substituent chemical shift of *ortho*-hydrogen atoms and *para*-hydrogen atoms in disubstituted carbazoles (unsymmetrical and symmetrical disubstituted carbazoles) is affected or not by the presence of another substituent attached to the carbazole moiety, we correlated the SCS values of disubstituted carbazoles with the SCS values of monosubstituted carbazoles. Figure 2 shows a linear correlations obtained for *ortho* and *para*-hydrogen atoms. The slope values are as follows: *ortho*-hydrogens (2-H, 4-H, 5-H and 7-H) 1.13 (r^2 : 0.972), *para*-hydrogens (4-H) 1.43 (r^2 : 0.999). Evidently, these values, which are clearly greater than 1.00, suggest that the presence of another substituent attached to the carbazole moiety affects significantly the chemical shift of the *para*-hydrogen atoms rather than the chemical shift of the *ortho*-hydrogen atoms.

Correlation of ^{13}C NMR chemical shifts.

Table IV contains the ^{13}C chemical shift assignments for the substituted carbazoles in Series 1-5 and Table V contains the substituent induced chemical shift effects at each

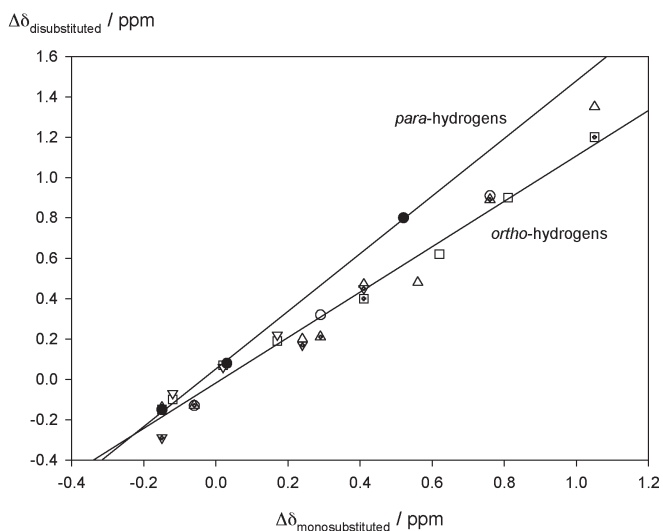


Figure 2. ^1H -SCS of disubstituted carbazoles ($\Delta\delta_{\text{disubstituted}}$) and ^1H -SCS of monosubstituted carbazoles ($\Delta\delta_{\text{monosubstituted}}$) correlation. Filled symbols: *para*-hydrogen atoms; unfilled symbols: *ortho*-hydrogens. Full lines: best linear regressions.

Table V
Observed substituent effects on ^{13}C chemical shifts of the substituted ring of carbazoles [a]

Compound	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
2	5.7 (1-C)	1.3 (2-C); 0.9 (9a-C)	1.8 (3-C); 2.6 (4a-C)	- 0.7 (4-C)
3	5.0 (3-C)	0.9 (2-C); 0.4 (4-C)	2.2 (1-C); 0.4 (4a-C)	- 1.2 (9a-C)
4	5.5 (1-C)	1.0 (2-C); 1.0 (9a-C); 5.3 (6-C)	0.4 (3-C); 0.5 (4a-C); - 0.8 (4b-C); 0.4 (8-C)	- 0.6 (4-C); - 1.2 (8a-C)
5	4.6 (3-C; 6-C)	0.6 (2-C; 7-C); 0.7 (4-C; 5-C)	1.7 (1-C; 8-C); 0.2 (4a-C; 4b-C)	- 0.9 (9a-C; 8a-C)
8	- 8.3 (1-C)	2.5 (2-C); (9a-C)	2.2 (3-C); (4a-C)	- 0.5 (4-C)
9	- 7.9 (3-C)	2.5 (2-C); 3.2 (4-C)	2.0 (1-C); 2.0 (4a-C)	- 1.0 (9a-C)
10	- 7.6 (3-C; 6-C)	3.2 (2-C; 7-C); 3.7 (4-C; 5-C)	2.1 (1-C; 8-C); (4a-C; 4b-C)	-0.9 (9a-C; 8a-C)
13	- 38.2 (1-C)	8.7 (2-C); 2.0 (9a-C)	1.6 (3-C); 0.6 (4a-C)	1.0 (4-C)
14	- 37.2 (3-C)	8.0 (2-C); 9.2 (4-C)	2.5 (1-C); 2.7 (4a-C)	- 0.7 (9a-C)
15	- 37.8 (1-C)	9.5 (2-C); - 0.8 (9a-C); - 37.6 (6-C)	2.4 (3-C); - 0.7 (4a-C); 3.1 (4b-C); 3.3 (8-C)	1.1 (4-C); - 0.8 (8a-C)
16	- 36.7 (3-C; 6-C)	8.7 (2-C; 7-C); 9.7 (4-C; 5-C)	2.7 (1-C; 8-C); 2.6 (4a-C; 4b-C)	1.4 (9a-C); - 0.6 (8a-C)
18	9.3 (1-C)	0.3 (2-C); 0 (9a-C)	0.9 (3-C); 0.9 (4a-C)	7.1 (4-C)
19	10.1 (3-C)	4.3 (2-C); 1.5 (4-C)	1 (1-C); 0.9 (4a-C)	0 (9a-C)
20	11.6 (3-C; 6-C)	2.6 (2-C; 7-C); 4.5 (4-C; 5-C)	-0.2 (1-C; 3-C); -0.3 (4a-C; 4b-C)	- 1.1 (9a-C); 0.4 (8a-C)
21	29.8 (1-C)	- 3.7 (2-C); - 7.8 (9a-C)	9.5 (3-C); 8.5 (4a-C)	13.3 (4-C)
22	24.7 (3-C)	- 4.2 (2-C); - 2.5 (4-C)	0.9 (1-C); - 0.2 (4 ^a -C)	1.4 (9a-C)
23	21.6 (1-C); 25.6 (6-C)	- 5.4 (2-C); - 7.3 (9a-C); - 2.9 (5-C); - 2.7 (7-C)	4.8 (3-C); 2.2 (4a-C); - 1 (4b-C); 2.1 (8-C)	9.8 (4-C); - 10.4 (8a-C)
24	31.4 (3-C; 6-C)	- 2.5 (2-C; 7-C); - 0.4 (4-C; 5-C)	1.6 (1-C; 8-C); 0.3 (4a-C; 4b-C)	1.6 (9a-C; 8a-C)

[a] Positive values indicate downfield shifts.

carbon atom. These substituent effects are tabulated according to the spatial relationship between the carbon atom in question and the substituent (*ipso*, *ortho*, *meta* and *para*). In Table V we also distinguish those carbon atoms, which are already bearing a substituent.

The ^{13}C substituent chemical shift values at the *ipso* carbon atoms of bromo, iodo and nitro substituted carbazoles are enhanced compared to that of mono substituted benzenes while chlorocarbazoles (Series 1) and benzoylcarbazoles (Series 4) show ^{13}C substituent chemical shift values that are similar and in the same order of magnitude as in mono substituted benzene derivatives [11]. From the values shown in Table V a deshielding effect on the *ipso*-carbon is observed for compounds **2**, **3**, **4** and **5** (Series 1) due to the resonance effect of the substituent. In the case of 1,3,6-trichlorocarbazole and 1,3,6,8-tetrachlorocarbazole (Series 1) the deshielding effect at the *ipso*-carbon diminishes slightly, meaning that the inductive effect begins to operate when the number of chlorine atoms attached to the carbazole moiety are higher than two and hence, overshadows the resonance effect. A shielding effect (upfield shift) on the chemical shift at the *ipso*-carbon of bromo and iodo substituted carbazoles (Series 2 and 3, respectively) is observed. This effect is due to a strong inductive effect, which prevails over the resonance effect. A long carbon-halogen bond (C-X; X: Br and I), a high molecular volume of bromo and iodo groups and the electronegativity of these atoms account for this behaviour. From Table V we can conclude that a deshielding effect

(downfield shift) is observed for nitro and benzoyl groups attached to the carbazole moiety (Series 4 and 5). This behaviour means that a withdrawing resonance effect (-R) operates due to a coplanarity between the carbazole moiety and the nitro and benzoyl groups, respectively.

The substituent chemical shift values of unsubstituted *ortho*-carbon atoms of carbazoles in Series 1-5 are of similar magnitude and sign compared to that of monosubstituted benzene derivatives (see Table V). For compounds **2** - **20** a deshielding effect is observed while a shielding effect is observed for compounds **21** - **24**. Inductive and resonance effects account for these behaviours. Those *ortho*-carbon atoms such as 9a-C or 8a-C, which are already bearing a substituent, do not reveal any consistent patterns (see Table V).

The ^{13}C chemical shifts of the *meta*-carbons of carbazoles in Series 1-5 span a range of only 2.2 ppm. These carbon atoms are far enough removed from the substituent to preclude appreciable magnetic effects of the "neighbour-anisotropy" type or of intramolecular dispersion effects [11]. It would seem that these small variations could be interpreted in terms of the influence of inductive effects on the electronic environment of the *meta* carbon and on the change in the aromatic ring current brought about by the presence of the substituent. Similar results are observed in mono substituted benzene derivatives [11].

The substituent chemical shift values of the unsubstituted *para*-carbon atoms (4-C) of carbazoles in Series 1-5

are of similar magnitude and sign compared to that of monosubstituted benzene derivatives. For compounds **2** - **10** a deshielding effect is observed while a shielding effect is observed for compounds **11** - **24**. Inductive and resonance effects account for these behaviours. Those *ortho*-carbon atoms such as 9a-C or 8a-C, which are already bearing a substituent, do not reveal any consistent patterns (see Table V) because these values span a range of only 2.8 ppm compared to those unsubstituted *para*-carbon atoms (span of chemical shift of 14 ppm).

We also performed the Lynch correlations in order to estimate quantitatively the influence of the substituent chemical shift of *ipso*, *ortho*, *meta* and *para*-carbon atoms in Series 1 - 5. For *ipso*-carbon atoms (1-C, 3-C and 6-C) of carbazoles in Series 1 - 5 the Lynch correlations afford good linear plots even though few numbers of substituent groups (Cl, Br, I, CPh and NO₂) are used for this analysis and the results are shown in Table VI. The slope values obtained for the *ortho*-carbon atoms are between 1.17 and 1.25 with a correlation factor (*r*²) greater than 0.99. The data clearly reveal that the chemical shifts of *ipso*-carbon atoms in the carbazole moiety are influenced to a larger extent than the monosubstituted benzenes by the variable substituent. A similar behaviour was observed for the chemical shift of unsubstituted *para*-carbon atoms (4-C) in 1-substituted and 1,6-disubstituted carbazoles (see Table VI). The Lynch correlations of unsubstituted *ortho*-carbon atoms (2-C, 4-C, 5-C and 7-C) of carbazoles in Series 1 - 5 afford slope values that range between 0.77 and 0.97 and are smaller than 1.00 suggesting that the substituent effect

is transmitted to a lesser extent in the carbazole moiety than in monosubstituted benzenes. *Ortho*- and *para*-substituted carbon atoms, such as 9a-C and 8a-C do not show correlation as evidenced by a significant spread of the data. Also, for *meta*-carbons no Lynch correlation was observed.

Also, we verified that the substituent chemical shift of ¹³C in tri- and tetrahalogenated carbazoles (Series 1, 2 and 3) is strictly additive. We calculated the substituent chemical shift at the *ipso*-carbon atoms of compounds **6**, **7**, **11**, **12** and **17** using carbazole (compound **1**, Series 1) as the reference and these values were defined as $\Delta\delta_{\text{EXP}}$. Then, we calculated the expected substituent chemical shift for compounds **6**, **7**, **11**, **12** and **17** by adding the substituent chemical shift observed for mono halogenated carbazoles and the new values were defined as $\Delta\delta_{\text{THEO}}$. Figure 3 shows the linear correlations obtained for *ipso*-carbon atoms between experimental ($\Delta\delta_{\text{EXP}}$) and calculated ($\Delta\delta_{\text{THEO}}$). The slope values obtained was 1.03 (*r*²: 0.988) which suggest that the substituent ¹³C chemical shift is additive.

Charge Density and Chemical Shifts.

We calculated the net atomic charge density of carbazoles in Series 1 - 5 by using the semi empirical PM3 method. Taking into account that there is a linear relationship between the measured ¹³C chemical shift and the net atomic charge density, we attempted to correlate the ¹³C chemical shifts of carbon atoms at *ipso*, *ortho*, *meta* and *para* positions and the net atomic charge on the same carbon atoms in carbazoles of Series 1 - 5. The net atomic

Table VI
Lynch correlations of ¹³C chemical shifts of substituted carbazoles.

	1-substituted carbazoles		3-substituted carbazoles		<i>Ips</i> o-position 3,6-substituted carbazoles		1,6-substituted carbazoles	
	1-C		3-C		3-C / 6-C		1-C	6-C
Slope	1.25		1.17		1.19		1.23	1.20
<i>r</i> ²	0.991		0.997		0.996		0.992	0.997

	1-substituted carbazoles		3-substituted carbazoles		<i>Ortho</i> -position 3,6-substituted carbazoles			1,6-substituted carbazoles		
	2-C	9a-C	2-C	4-C	2-C 7-C	4-C 5-C	2-C	9a-C	5-C	7-C
Slope	0.81	No correlation	0.79	0.79	0.73	0.91	0.97	No correlation	0.85	0.77
<i>r</i> ²	0.985		0.995	0.973	0.953	0.996	0.994		0.984	0.985

	<i>Para</i> -position	
	1-Substituted carbazole	1,6-Substituted carbazole
	4-C	4-C
Slope	1.73	1.35
<i>r</i> ²	0.944	0.964

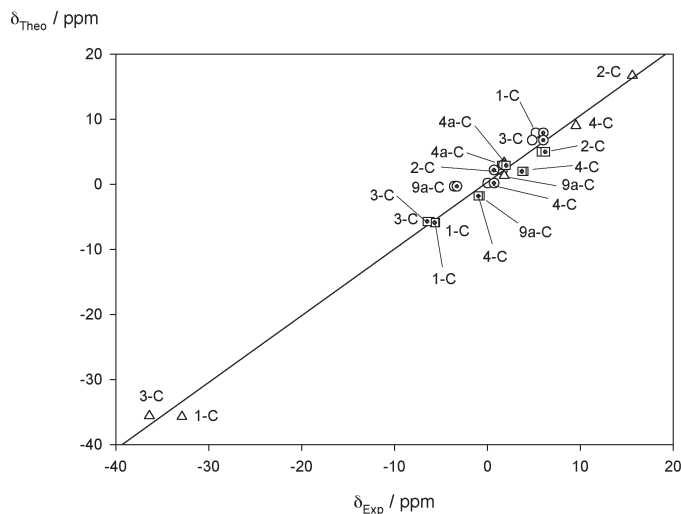


Figure 3. Correlation between the theoretical (δ_{Theo}) and experimental (δ_{Exp}) ^{13}C chemical shifts of polysubstituted carbazoles in Series 1, 2 and 3: Δ 1,6-dichlorocarbazole; ∇ 3,6-dibromocarbazole; \blacksquare 1,6-diiodocarbazole; \square 1,3,6,8-tetrachlorocarbazole; \circ 1,3,6,8-tetrabromocarbazole. Full line: best linear regression.

charge density values of carbazoles in Series 1 - 5, computed by PM3 calculations, are shown in Table VII.

The ^{13}C chemical shifts at *para* position have been correlated to the net atomic charge density on the same carbon atoms in carbazoles of Series 1 - 5. In this analysis we distinguish the *para*-carbon atoms bearing a substituent (9a-C and 8a-C) and unsubstituted *para*-carbon atoms (4-C). Figure 4 shows the two linear dependences between the ^{13}C chemical shifts of 9a-C, 8a-C and 4-C and the net atomic charge density on the same carbon atoms of carbazoles in Series 1 - 5. Taking into account that the number of substituents used for the correlation analysis is only 6, the results show that the net atomic charge density nicely predicts the linear trend with the substituent effect on the ^{13}C chemical shifts of *para*-carbons in carbazoles of Series 1 - 5. Interestingly the slope of the correlation of carbon 4-C is greater than that of carbons 8a-C and 9a-C suggesting that the substituent effect is channelled predominantly to the unsubstituted *para*-carbon atom (4-C) rather than to the *para*-carbons 8a-C and 9a-C, respectively (e.g., the slope for atom 4-C is 162.1 (r^2 : 0.911) and for atoms 9a-C and 8a-C the slope is 69.8 (r^2 : 0.905)).

The ^{13}C chemical shifts at the *ortho* position were also correlated with the net atomic charge density on the same carbon atoms in carbazoles of Series 1 - 5. These *ortho*-carbon atoms are classified into substituted (9a-C) and unsubstituted (2-C, 4-C, 5-C and 7-C). Figure 5 shows the

Table VII
Net Atomic Charge Density Values of polysubstituted carbazoles [a]

	1	2	3	4	5	6	7	8	9	10	11	12
1-C	-0.123	-0.133	-0.095	-0.134	-0.095	-0.124	-0.125	-0.131	-0.116	-0.101	-0.123	-0.124
2-C	-0.074	-0.082	-0.084	-0.079	-0.081	-0.083	-0.081	-0.055	-0.058	-0.061	-0.038	-0.035
3-C	-0.138	-0.116	-0.116	-0.115	-0.146	-0.139	-0.139	-0.135	-0.141	-0.133	-0.137	-0.138
4-C	-0.040	-0.049	-0.050	-0.046	-0.047	-0.048	-0.046	-0.032	-0.019	-0.025	-0.017	-0.015
5-C		-0.047	-0.046	-0.048		-0.045		-0.039	-0.038		-0.023	
6-C		-0.126	-0.125	-0.147		-0.147		-0.135	-0.135		-0.134	
7-C		-0.079	-0.079	-0.081		-0.079		-0.135	-0.072		-0.058	
8-C		-0.107	-0.107	-0.094		-0.094		-0.073	-0.120		-0.100	
4a-C	-0.078	-0.056	-0.055	-0.059	-0.058	-0.047	-0.050	-0.076	-0.074	-0.064	-0.063	-0.065
4b-C		-0.070	-0.070	-0.059		-0.062		-0.078	-0.078		-0.066	
9a-C	-0.119	-0.121	-0.118	-0.120	-0.120	-0.119	-0.123	-0.104	-0.116	-0.116	-0.099	-0.101
8a-C		-0.117	-0.121	-0.121		-0.124		-0.121	-0.120		-0.117	
	13	14	15	16	17	18	19	20	21	22	23	24
1-C	-0.150	-0.118	-0.151	-0.116	-0.146	-0.179	-0.122	-0.112	-0.446	-0.148	-0.438	-0.134
2-C	-0.054	-0.053	-0.052	-0.052	-0.034	-0.039	-0.042	-0.037	0.022	0.014	0.029	0.013
3-C	-0.135	-0.159	-0.133	-0.160	-0.158	-0.148	-0.190	-0.169	-0.167	-0.458	-0.059	-0.440
4-C	-0.035	-0.016	-0.034	-0.014	-0.018	-0.019	0.010	-0.021	0.023	0.068	0.028	0.064
5-C	-0.039	-0.038	-0.015		-0.021	-0.048	-0.048	-0.004	-0.046	-0.041	0.063	
6-C	-0.136	-0.135	-0.159		-0.154	-0.126	-0.122	-0.170	-0.119	-0.121	-0.443	
7-C	-0.073	-0.072	-0.052		-0.055	-0.080	-0.081	-0.057	-0.076	-0.073	0.011	
8-C	-0.119	-0.121	-0.115		-0.102	-0.105	-0.105	-0.109	-0.099	-0.109	-0.128	
4a-C	-0.078	-0.075	-0.078	-0.075	-0.065	-0.087	-0.083	-0.071	-0.104	-0.113	-0.101	-0.101
4b-C	-0.079	-0.078	-0.076		-0.067	-0.048	-0.048	-0.073	-0.071	-0.066	-0.109	
9a-C	-0.098	-0.118	-0.120	-0.119	-0.095	-0.059	-0.097	-0.106	-0.022	-0.071	-0.035	-0.081
8a-C	-0.121	-0.120	-0.099		-0.119	-0.121	-0.123	-0.106	-0.131	-0.132	-0.083	

[a] Computed by semi empirical PM3 calculations.

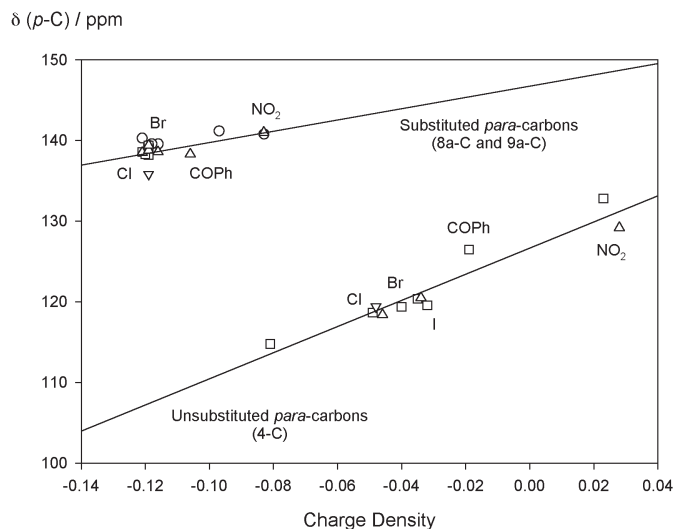


Figure 4. Correlations between ^{13}C chemical shifts at unsubstituted (4-C) and substituted (9a-C and 8a-C) *para*-carbon atoms and net atomic charge density at the same carbon atoms of carbazoles: – 1-substituted carbazoles; ∇ 3-substituted carbazoles; \circ 3,6-disubstituted carbazoles and X 1,6-disubstituted carbazoles. Full line: best linear regression.

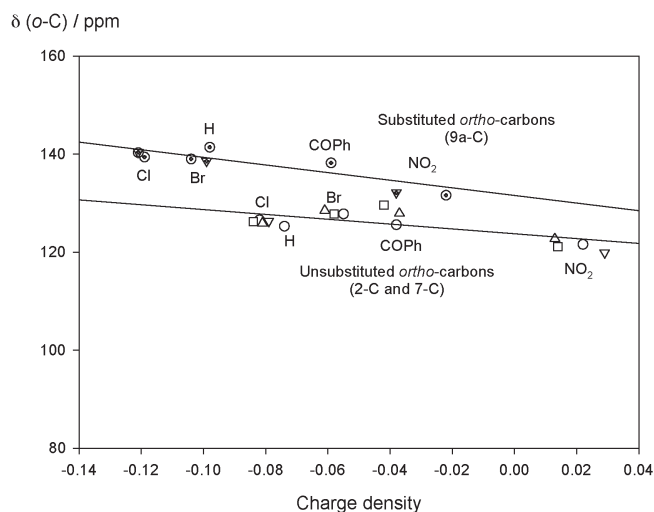


Figure 5. Correlations between ^{13}C chemical shifts at unsubstituted (2-C and 7-C) and substituted (9a-C) *ortho*-carbon atoms and net atomic charge density at the same carbon atoms of carbazoles: – 1-substituted carbazoles; ∇ 3-substituted carbazoles; \circ 3,6-disubstituted carbazoles and X 1,6-disubstituted carbazoles. Full line: best linear regression.

two linear dependences between the ^{13}C chemical shifts of 9a-C, 2-C, 4-C, 5-C and 7-C and the net atomic charge density on the same carbon atoms of carbazoles in Series 1 - 5. A linear regression analysis gave a slope of -77.3 (r^2 : 0.754) for unsubstituted *ortho*-carbon atoms (2-C, 4-C, 5-C and 7-C) and a slope of -49.3 (r^2 : 0.889) for substituted *ortho*-carbon atoms (9a-C). These values suggest that the

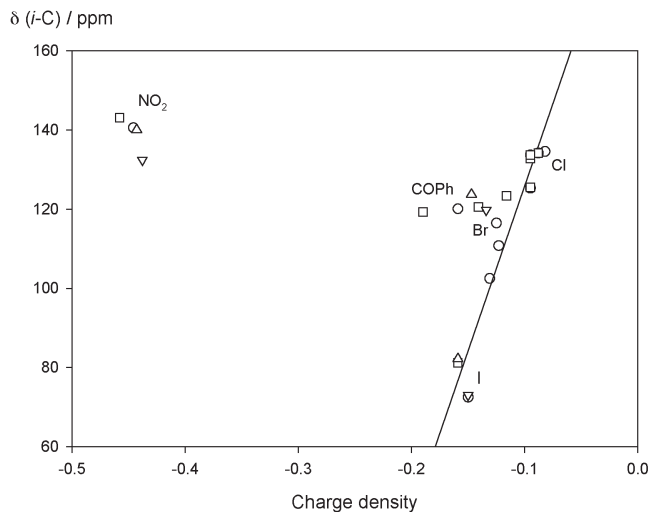


Figure 6. Correlations between ^{13}C chemical shifts at *ipso*-carbon atoms (1-C, 3-C and 6-C) and net atomic charge density at the same carbon atoms of carbazoles: – 1-substituted carbazoles; ∇ 3-substituted carbazoles; \circ 3,6-disubstituted carbazoles and X 1,6-disubstituted carbazoles. Full line: best linear regression.

substituent effect is also transmitted to substituted *ortho*-carbon atoms to a greater extent than to the unsubstituted *ortho*-carbon atoms.

Finally, we have also attempted the correlation of the ^{13}C chemical shifts at the *ipso*-position of carbazoles in Series 1 - 5 with the net atomic charge density at the same carbon atoms. Figure 6 shows satisfactorily linear correlation when the nitro group is excluded from the correlation analysis due to its deviation from linearity. This deviation suggests a redistribution of the electron density on the carbazole moiety due to the influence of the nitro group, a strong withdrawing substituent. Thus, the presence of a nitro group attached to the carbazole moiety can lead to an increased contribution of the dipolar resonance structures as it is illustrated for 3-nitrocarbazole in Figure 7.

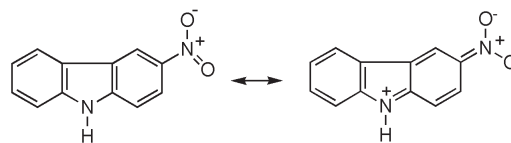


Figure 7. Dipolar resonance structure of 3-nitrocarbazole.

Analysis of the ^1H chemical shifts of carbazoles in Series 1 - 5 shows that the variable substituent affects significantly the *ortho*- and *para*-hydrogen atoms. These hydrogen atoms give good linear Lynch correlations while *meta*-hydrogen atoms do not. In general, the chlorine substituent

effect on *ortho* and *para*-hydrogen atoms shows a uniformly upfield shift (shielding effect) while iodine, benzoyl and nitro substituent effects show a uniformly downfield shift (deshielding effect). In the case of bromine atom the substituent effect at the *ortho*-hydrogen atom shows a downfield shift (deshielding effect) while for *para*-hydrogen atoms a shielding effect is observed. These behaviours could be ascribed to inductive and resonance effects.

The variable substituent affects significantly the ^{13}C -NMR chemical shifts of the *ipso*, *ortho* and *para*-carbon atoms of carbazoles in Series 1 – 5 and Lynch correlations of these carbon atoms give satisfactorily linear regression analysis. The substituent effect on *ipso* and *para*-carbon atoms shows a uniformly shielding effect (upfield shift) for the chlorine atom while a deshielding effect (downfield shift) is observed for iodine, benzoyl and nitro groups. The substituent effect on *ortho*-carbon atoms shows an upfield shift for chlorine, bromine, iodine and benzoyl groups while a deshielding effect (downfield shift) is observed for the nitro group. Also, we verified that the substituent ^{13}C chemical shift in tri- and tetra-halogenated carbazoles (Series 1, 2 and 3) is strictly additive.

The ^{13}C chemical shifts of carbon atoms at *ipso*, *ortho* and *para* position and the net atomic charge density computed by PM3 calculations at the same atoms for carbazoles in Series 1 - 5 give good linear correlations and hence, the charge density nicely predicts the substituent effect on the ^{13}C NMR chemical shifts of the compounds studied. Also, this relationship can be employed for the estimation of the ^{13}C chemical shifts using the net atomic charge density data or *vice versa*.

EXPERIMENTAL

Carbazole was purchased from Aldrich and was recrystallized from ethanol. 1-Benzoylcarbazole, 3-benzoylcarbazole, 3,6-dibenzoylcarbazole, 1-chlorocarbazole, 3-chlorocarbazole, 1,6-dichlorocarbazole, 3,6-dichlorocarbazole, 1,3,6-trichlorocarbazole and 1,3,6,8-tetrachlorocarbazole, 1-bromocarbazole, 3-bromocarbazole, 1,6-dibromocarbazole, 3,6-dibromocarbazole, 1,3,6-tribromocarbazole, 1,3,6,8-tetrabromocarbazole, 1-nitrocarbazole, 3-nitrocarbazole, 1,6-dinitrocarbazole, 3,6-dinitrocarbazole, 1-iodocarbazole, 3-iodocarbazole, 1,6-diiodocarbazole, 3,6-diiodocarbazole and 1,3,6-triiodocarbazole were prepared according to the literature procedures [6].

The ^1H NMR spectra were obtained at 200 MHz (Bruker spectrometer) for approximately 0.03 M solutions with TMS as inter-

nal reference. Broadband and off-resonance decoupled ^{13}C spectra were obtained with the same instrument for *ca* 0.5 M solutions with TMS as internal reference. The spectra of all the compounds were measured in CDCl_3 except for 1,6-dinitrocarbazole and 3,6-dinitrocarbazole (Series 4) where $\text{DMSO}-d_6$ was employed to overcome solubility difficulties. A pulse angle of 37.5° (5 μs) and a repetition time of 3.7 s were used for benzoyl carbazole derivatives at room temperature (20 – 21 $^\circ\text{C}$). 2D nmr C/H shift correlated spectra were obtained using the standard Bruker program (HETCOR; Porgramme name: XHCORRDC.AUR) at 500 MHz with a spectral width of 2551.02 Hz in the ^1H direction (resolution 128 Hz per point) and 15151.52 Hz in the ^{13}C direction (resolution 2048 Hz per point).

The ground state geometry and static charge distribution of carbazoles in Series 1 to 5 were calculated by using the semi empirical parameterised PM3 method as implemented in version of the HyperChem Program [13] which has proven to be effective in studies of molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

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