On the Synthesis and Isolation of Chlorocarbazoles Obtained by Chlorination of N-Substituted Carbazoles

Sergio M. Bonesi and Rosa Erra-Balsells*

Departamento de Quimica Orgánica, Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires, cc 74- suc 30, 1430 - Buenos Aires, Argentina
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Chloro derivatives of N-methylcarbazole (1), N-phenylcarbazole (2), N-acetylcarbazole (3), N-benzoyl-carbazole (4) and 2-methoxy-N-methylcarbazole are synthesized. They are compounds **1a, 1b, 1c, 1d, 1e, 2a, 2b, 3a, 3b, 3c, 3d, 4a, 4b, 5a, 5b, 5c, 5d** and **5e**. Some of them are described for the first time. By using semiempirical PM3 method theoretical substituent effects on the chlorinating reaction are calculated. A chlorination mechanism of carbazoles and N-substituted carbazoles are compared.

In our previous publication [1] we described the synthesis of six chloro derivatives of carbazole and several new chloro derivatives of 2-acetoxy-, 2-hydroxy-, 3-bromo and 3-nitrocarbazole. As we are interested in the study of the photochemistry of azacarbazoles [2-8], carbazoles [9,10], chlorocarbazoles, N-acyl- and N-alkylcarbazoles [11-13] and especially in the photoinduced electron transfer processes in which they can be involved, we decided to study the photophysical properties of the chloro derivatives of the N-substituted carbazoles. Thus, to begin with we now report the synthesis and characterization of several N-acyl and N-alkyl substituted chlorocarbazoles prepared by direct chlorination of N-methyl- **1**, N-phenyl- **2**, N-acetyl- **3**, N-benzoyl- **4** and 2-methoxy-N-methylcarbazole (**5**) (Scheme 1, compounds: **1a, 1b, 1c, 1d, 1e, 2a, 2b, 3a, 3b, 3c, 3d, 4a, 4b, 5a, 5b, 5c, 5d** and **5e**).

As is known, polymers containing carbazolyl moieties are good electron donors and possess outstanding electrical and photoelectrical properties [14,15,16]. The presence of chlorine in the polymer structure is desired because it modifies their physical properties [17] but owing to the so called "heavy atom effect" [18] chlorine can modify the photophysical and as a consequence the photoelectrical properties of the polymer.

The described chlorination of N-methylcarbazole with sulfuryl chloride provided a mixture of 3-chloro- and 3,6-dichloro-N-methylcarbazole in poor yield. Both chloro derivatives were only characterized by melting point and elemental analysis [19]. 3-Chloro-N-acetylcarbazole and 3,6-dichloro-N-acetylcarbazole were prepared by acetylation of the corresponding chlorocarbazoles and were characterized only by their melting points, elemental analysis and ir spectra [20,21]. M. de Rosa *et al.* [22] have described a procedure to obtain chlorocarbazoles by direct chlorination of carbazoles. The authors using only [1]H-nmr spectroscopy determined the composition of the mixture and the structure of the chlorinated products after direct N-methylation of the reaction mixture not attempting to isolate and purify the chloro derivatives obtained. In
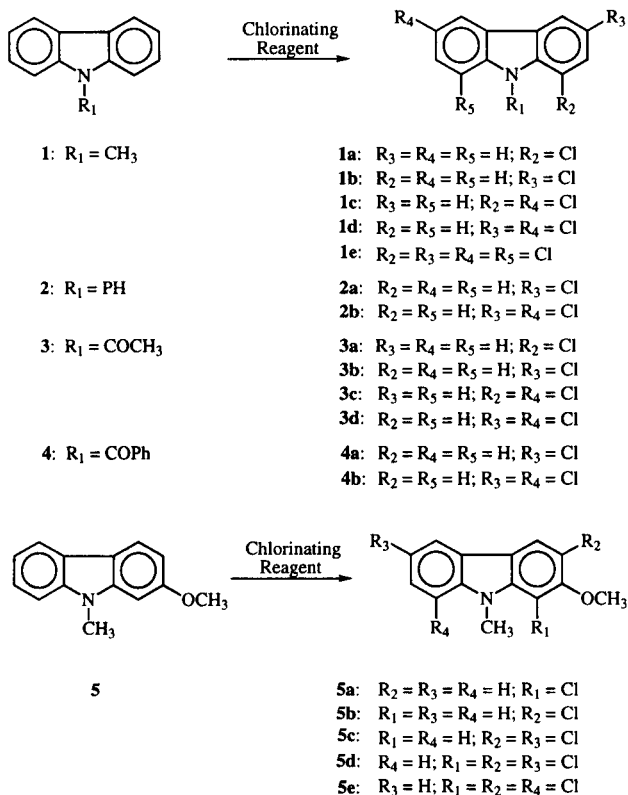
the same paper the authors have reported the synthesis of 3,6-dichloro-N-methylcarbazole by direct chlorination of N-methylcarbazole with two equivalents of N-chlorobenzotriazole and only the melting point and the chemical shift of the methyl group of this compound were reported. Although, 1,6-dichloro-N-methylcarbazole was also obtained by chlorination of l-chloro-N-methylcarbazole with one equivalent of N-chlorobenzotriazole which was surprisingly characterized only by the chemical shift (nmr) of the methyl group. Previously, Johnson used isotope dilution to characterize in the reaction mixture the products obtained by direct chlorination of N-acetylcarbazole [21].

As far as we know the direct chlorination of N-phenylcarbazole (**2**), N-benzoylcarbazole (**4**) and 2-methoxy-N-methylcarbazole (**5**) has not been described. Furthermore, several of the corresponding chloro derivatives of these carbazoles have not been previously described.

This study reports the preparation of chloro derivatives from N-alkylcarbazoles (Scheme 1, N-methylcarbazole (**1**), N-phenylcarbazole (**2**) and 2-methoxy-N-methylcarbazole (**5**)) and N-acylcarbazoles (Scheme 1, N-acetylcarbazole (**3**) and N-benzoylcarbazole (**4**)) using different chlorination reagents providing for the first time chlorocarbazoles **1e, 2a, 2b, 3a, 3c, 3d, 4a, 4b, 5a, 5b, 5c, 5d** and **5e** (Scheme 1). We also describe the use of several chromatographic methods (tlc, gc, gc-ms and column chromatography) in order to (i) follow the chlorination reaction; (ii) determine the yields of the reactions and (iii) isolate for complete characterization (elemental analysis, R_f, t_R, mp, uv, [1]H-nmr, ^{13}C-nmr and ms) the chloro derivatives obtained.

We also illustrate N-chlorobenzotriazole and N-chlorobenzotriazole-silica gel as a convenient new reagent systems for the high yield chlorination of carbazole to prepare mono-, di- and poly-chlorinated products depending on the stoichiometry used. Additionally, computational chemistry has been used to calculate the atomic charge density values. Those for the more relevant atoms are col-

Scheme 1

1: R₁ = CH₃ → 1: $R_1 = CH_3$

1a: $R_3 = R_4 = R_5 = H; R_2 = Cl$
1b: $R_2 = R_4 = R_5 = H; R_3 = Cl$
1c: $R_3 = R_5 = H; R_2 = R_4 = Cl$
1d: $R_2 = R_5 = H; R_3 = R_4 = Cl$
1e: $R_2 = R_3 = R_4 = R_5 = Cl$

2: $R_1 = PH$

2a: $R_2 = R_4 = R_5 = H; R_3 = Cl$
2b: $R_2 = R_5 = H; R_3 = R_4 = Cl$

3: $R_1 = COCH_3$

3a: $R_3 = R_4 = R_5 = H; R_2 = Cl$
3b: $R_2 = R_4 = R_5 = H; R_3 = Cl$
3c: $R_3 = R_5 = H; R_2 = R_4 = Cl$
3d: $R_2 = R_5 = H; R_3 = R_4 = Cl$

4: $R_1 = COPh$

4a: $R_2 = R_4 = R_5 = H; R_3 = Cl$
4b: $R_2 = R_5 = H; R_3 = R_4 = Cl$

5

5a: $R_2 = R_3 = R_4 = H; R_1 = Cl$
5b: $R_1 = R_3 = R_4 = H; R_2 = Cl$
5c: $R_1 = R_4 = H; R_2 = R_3 = Cl$
5d: $R_4 = H; R_1 = R_2 = R_3 = Cl$
5e: $R_3 = H; R_1 = R_2 = R_4 = Cl$

N-Methylcarbazole (**1**) was treated according to the general procedure described in the Experimental with one to four equivalents of *N*-chlorobenzotriazole whether or not in the presence of silica gel, at room temperature. The yields of the products were determined by gc after an appropriate time. The results are presented in Table I. As can be seen in this table (entry 1) this reaction provided a simple synthesis of 3-chloro-*N*-methylcarbazole (**1b**) (molar ratio 1:1) together with significant amounts of 1-chloro-*N*-methylcarbazole (**1a**) and 3,6-dichloro-*N*-methylcarbazole (**1d**). Production of **1d** was fairly clean when two equivalents of *N*-chlorobenzotriazole were used and a significant amount of 1,6-dichloro-*N*-methylcarbazole (**1c**) was also obtained (see Table I, entry 3). When four equivalents of *N*-chlorobenzotriazole were used 1,3,6,8-tetrachloro-*N*-methylcarbazole (**1e**) was obtained in high yield (see Table I, entry 5).

The chlorination reaction of **1** was also carried out with *N*-chlorobenzotriazole in the presence of silica gel (see Table I, entries 2 and 4). As it can be seen the presence of silica gel in the reaction medium was not beneficial because the reaction became slower and as a consequence, the product yields were considerably lower. According to this fact we observed that the monochlorinated products **1a** and **1b** predominated over the dichlorinated products **1c** and **1d**.

N-Phenylcarbazole (**2**) is rather less reactive than *N*-methylcarbazole (**1**). Thus, the chlorination reaction

Table I

Chlorination Reaction of *N*-Methylcarbazole (**1**) by Using *N*-Chlorobenzotriazole

Experiment No.	Molar Ratio	Silica-gel (g)	Time (minutes)	Products (%) [a]					
				1	**1a**	**1b**	**1c**	**1d**	**1e**
1	1:1	-	10	13	11	66	1.6	8.4	-
2	1:1	2	25	46	9.7	41	0.7	2.9	-
3	1:2	-	5	-	4	1.3	26	81	-
4	1:2	2	12	8.3	11	48	7.3	26	-
5	1:4	-	30	-	-	-	-	-	90

[a] Quantitative gc (HP-17) analysis.

lected in Tables VI, VII, VIII, IX and X and they are of use to discuss the reactivity of carbazoles **1-5**.

Results and Discussion.

In order to investigate the chlorination reactions of carbazoles **1-5** and taking into account the high reactivity of the carbazole [1] a standard set of experimental conditions was adopted. Thus, the solvent chosen as reaction medium was chloroform and depending on the substrate employed, the chlorination reaction was run at room temperature, at 55° or heating at reflux the reaction mixture to get a high yield of the chlorocarbazole derivatives.

Table II

Chlorination Reaction of *N*-Phenylcarbazole (**2**) by Using *N*-Chlorobenzotriazole

Experiment No.	Molar Ratio	Silica-gel (g)	Time (minutes)	Products (%) [a]		
				2	**2a**	**2b**
1	1:1	-	50	7.8	70	17
2	1:1	2	45	54	37	1.6
3	1:2	-	25	-	14	84

[a] Quantitative gc (HP-17) analysis.

was carried out at 25° and at 55° during longer periods of time. As can be seen in the Table II (entry 1), this reaction provided a simple synthesis of 3-chloro-N-phenylcarbazole (2a) together with significant amounts of 3,6-dichloro-N-phenylcarbazole (2b). When the reaction was carried out in the presence of silica gel (see Table II, entry 2) the reaction rate was diminished resulting in a lower yield of the 3,6-dichloro derivative 2b. Production of 2b was clean when two equivalents of N-chlorobenzotriazole were used and significant amounts of 2a was also obtained (see Table II, entry 3). We also performed the above reaction in the presence of silica gel but we could not improve the percentage yield of the mono- and dichlorinated products.

poor yield. As we mentioned above, when the chlorination was carried out in the presence of silica gel, there is no change in the product yields. It is noteworthy to mention that the introduction of a withdrawing N-substituent (acetyl or benzoyl group), modifies the reactivity of the carbazole moiety towards the electrophilic substitution chlorination reaction. Thus, longer periods of reaction time (hours) are necessary to obtain a high conversion of the starting substrate. In contrast after the introduction of a donor N-substituent such as methyl or phenyl group, a shorter period of time (minutes) is sufficient to obtain a high conversion of the starting carbazole.

We also studied the chlorination reaction of 2-methoxy-N-methylcarbazole (5) according to the general procedure

Table III

Chlorination Reaction of N-Acetylcarbazole by Using N-Chlorobenzotriazole
and N-Chlorosuccinimide

Experiment No.	Molar Ratio [b]	Molar Ratio [c]	Silica-gel (g)	Time (hours)	Products (%) [a]			
					3	3a	3b	3c
1	1:1	-	-	8	10	-	65	25
2	1:1	-	2	10	18	0.8	60	22
3	-	1:1	-	12	24	-	66	11
4	-	1:1	2	10	8.9	-	70	20
5	1:2	-	-	5	-	-	15	86

[a] Quantitative gc (HP-17) analysis; [b] N-Chlorobenzotriazole chlorinating reagent used; [c] N-Chlorosuccinimide chlorinating reagent used.

Table IV

Chlorination Reaction of N-Benzoylcarbazole by Using N-Chlorobenzotriazole
and N-Chlorosuccinimide

Experiment No.	Molar Ratio [b]	Molar Ratio [c]	Silica-gel (g)	Time (hours)	Products (%) [a]		
					4	4a	4b
1	1:1	-	-	12	28	69	-
2	1:1	-	2	16	73	25	0.7
3	-	1:1	-	12	36	64	0.9
4	-	1:1	2	15	39	58	1.9
5	1:2	-	-	8	12	12	76

[a] Quantitative gc (HP-17) analysis; [b] N-Chlorobenzotriazole chlorinating reagent used; [c] N-Chlorosuccinimide chlorinating reagent used.

The chlorination reaction of N-acetylcarbazole (3) and N-benzoylcarbazole (4) with N-benzotriazole were not so selective. Monochlorination of 3 and 4 produced the expected products, 3-chloro-N-acetyl- 3b and 3-chloro-N-benzoylcarbazole (4a) respectively, in good yield (see Table III and Table IV). However, in both reaction mixtures significant amounts of the corresponding 3,6-dichloro-N-acylcarbazoles 3d (Table III) and 4b (Table IV) were obtained. It is interesting to note that in both reactions the 1-chloro-N-acylcarbazoles were produced in

described in the Experimental. The yields of the products obtained (gc) are presented in Table V. As can be seen in this table the reaction conducted at 25° provided a simple synthesis of 3-chloro-2-methoxy-N-methylcarbazole (5b) when one equivalent of N-chlorobenzotriazole was used, together with significant amounts of 1-chloro-2-methoxy-N-methylcarbazole (5a). When the 5 to N-chlorobenzotriazole molar ratio was (1:2), 3,6-dichloro-2-methoxy-N-methylcarbazole (5c) was formed in a fairly good yield together with significant amounts of 5a and 5b (see

Table V

Chlorination Reaction of 2-Methoxy-*N*-methylcarbazole by Using *N*-Chlorobenzotriazole

Experiment No.	Molar Ratio	Temperature (°C)	Time (minutes)	Products (%) [a]					
				5	5a	5b	5c	5d	5e
1	1:1	-18	9	0	23	76	-	-	-
2	1:1	25	20	0	17	77	-	-	-
3	1:2	25	38	0	3.4	17	80	-	-
4	1:3	25	50	0	1.3	3.4	9.5	75	10

[a] Quantitative gc (HP-17) analysis.

Table V, entry 3). We also carried out these reactions at -18° but we could neither improve the percentage yield of the monochlorinated products nor the selectivity of the chlorination reaction (see Table V, entry 2). It is noteworthy to mention that the introduction of an electron donor substituent on the benzenic ring of the *N*-methylcarbazole (methoxy group) accelerates the reaction rate of the chlorination reaction of **5** compared with the rate of chlorination of *N*-methylcarbazole (**1**). The presence of a methoxy group as a substituent on the *N*-methylcarbazole moiety produces a noticeable change in the substitution pattern for compound **5** in comparison with that of the other carbazole derivatives studied in the present work, **1-4**.

Furthermore, as it was pointed out above, all these reactions were monitored by gc in order to obtain additional information about the mechanism of the chlorination reaction. From the kinetic profiles obtained for the chlorination reaction of **5** with one equivalent of *N*-chlorobenzotriazole, it can be concluded that **5a** and **5b** were formed in parallel reactions. When two equivalents of *N*-chlorobenzotriazole were used, **5b** was the primary product which in turn gave the 3,6-dichloro-2-methoxy-*N*-methylcarbazole (**5c**) as the main product of the chlorination reaction of **5**. Three equivalents of *N*-chlorobenzotriazole were also used and compound **5c**, 1,3,6-trichloro-2-methoxy-*N*-methylcarbazole (**5d**) and 1,3,8-trichloro-2-methoxy-*N*-methylcarbazole (**5e**) were formed and compound **5d** was the main product (see Table V, entry 4). Taking into account that the presence of silica gel in the medium during the chlorination reaction of **1** and **2** was not beneficial, we decided not to carry out the chlorination reacion of **5** with *N*-chlorobenzotriazole in the presence of silica-gel.

This differential reactivity of the carbazoles **1**, **2**, **3**, **4** and **5** towards the electrophilic substitution chlorination could be rationalized taking into account charge distribution. As is known the static charge distribution is frequently used for interpreting and predicting chemical reactivity and it should indicate sites of kinetic attack by incoming reagents. The net atomic charge values were calculated by using the semiempirical PM3 method as implemented in the version of the HyperChem release 4.5 program [23] to obtain the optimized geometry of the *N*-substituted carbazoles and their chloro derivatives.

In Tables VI, VII, VIII, IX and X, the static atomic charge density values calculated for compounds **1**, **2**, **3**, **4** and **5** are shown. These *N*-substituted carbazoles have the higher negative values localized at C-1, C-3, C-6 and C-8 and it would be expected that the incoming chlorine cation (Cl+) can preferentially attack these positions. It is worthwhile to point out that C-3 and C-6 have the highest negative charge density values compared to that of C-1 and C-8. According to our experimental results when the **1** to *N*-chlorobenzotriazole molar ratio was (1:1), 1-chloro-**1a** and 3-chloro-*N*-methylcarbazole (**1b**) were formed, **1b** being formed in a fairly good yield. These experimental results agrees with the conclusions obtained by analyzing the atomic static charge distribution for *N*-methylcarbazole. Although, when the chlorination reactions of *N*-phenyl- **1**, *N*-acetyl- **3** and *N*-benzoylcarbazole (**4**) with one equivalent of *N*-chlorobenzotriazole were carried out, again the 1-chloro- and 3-chloro-*N*-substituted carbazoles were substituted preferentially at C-3 of the carbazole moiety. Again, our experimental results for **2**, **3** and **4** are in agreement with the conclusions obtained by analyzing the atomic charge density distribution calculations by the semiempirical PM3 method.

Simultaneously, we have calculated the static charge density values by the semiempirical PM3 method for all the 1-chloro- and 3-chloro-substituted carbazoles and these values are presented in Tables VI to X. As can be seen in these tables the highest static charge density values are localized at C-6 for both series of 1-chloro- and 3-chloro-*N*-substituted carbazoles, and it is expected that the incoming second chlorine cation would attack at this position by means of the well-known electrophilic substitution to yield the dichloro-*N*-substituted carbazole. Experimentally, we performed the chlorination reaction of the *N*-substituted carbazole **1-5** with two equivalents of *N*-chlorobenzotriazole and 1,6-dichloro and 3,6-dichloro-*N*-substituted carbazoles were obtained as the main products together with significant amounts of the monochloro-

Table VI

Static Charge Distribution for *N*-Methylcarbazole (**1**) [a]

Compounds	1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
1	-0.108	-0.082	-0.126	-0.050					0.164
1a	-0.129	-0.088	-0.114	-0.052	-0.048	-0.125	-0.080	-0.106	0.178
1b	-0.096	-0.085	-0.146	-0.051	-0.047	-0.125	-0.079	-0.108	0.169
1c	-0.129	-0.085	-0.114	-0.049	-0.050	-0.146	-0.083	-0.094	0.183
1d	-0.096	-0.082	-0.147	-0.048					
1e	-0.117	-0.089	-0.136	-0.051					

[a] Calculations were performed using PM3 method [23].

Table VII

Static Charge Distribution for *N*-Phenylcarbazole (**2**) [a]

Compounds	1-C 11-C	2-C 12-C	3-C 13-C	4-C 14-C	5-C 15-C	6-C	7-C	8-C	9 (NH)
2	-0.117 -0.154	-0.085 -0.075	-0.126 -0.123	-0.048					
2a	-0.105 -0.152	-0.087 -0.075	-0.148 -0.121	-0.049	-0.045	-0.124	-0.082	-0.117	0.309
2b	-0.104 -0.151	-0.085 -0.075	-0.148 -0.118	-0.072					0.303

[a] Calculations were performed using PM3 method [23].

Table VIII

Static Charge Distribution for *N*-Acetylcarbazole (**3**) [a]

Compounds	1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
3	-0.125	-0.079	-0.121	-0.049	-0.054	-0.120	-0.084	-0.089	0.139
3a	-0.134	-0.082	-0.113	-0.049	-0.047	-0.123	-0.076	-0.105	0.092
3b	-0.116	-0.081	-0.144	-0.050	-0.050	-0.121	-0.081	-0.090	0.148
3c	-0.118	-0.087	-0.106	-0.053	-0.050	-0.143	-0.080	-0.106	0.117
3d	-0.113	-0.079	-0.144	-0.048	-0.053	-0.142	-0.084	-0.076	0.141

[a] Calculations were performed using PM3 method [23].

N-substituted carbazoles. It is noteworthy to mention that the 3,6-dichloro-*N*-substituted carbazoles were formed preferentially (see Tables I to V). Again, correlations between the atomic charge density values calculated and our experimental results were observed. Thus, it seems certain that eletrophilic attack of *N*-methyl-, *N*-phenyl-, *N*-acetyl- and *N*-benzoylcarbazole under a wide variety of reaction conditions occurs preferentially at the carbon atoms with charge density values higher than -0.100.

We also calculated the charge density values for 1,6-dichloro- **1c**, 3,6-dichloro- **1d**, 1,3,6-trichloro- and 1,3,6,8-tetrachloro-*N*-methylcarbazole (**1e**) and the results obtained are presented in Table V. These calculated values would readily explain the substitution pattern experimen-

tally obtained. As can be seen in Table I, when the **1** to *N*-chlorobenzotriazole molar ratio was (1:4), 1,3,6,8-tetrachloro-*N*-methylcarbazole was obtained as the main product together with significant amounts of 1,3,6-tri-chloro-*N*-methylcarbazole. Our experimental results are again in agreement with results predicted by semiempirical calculations.

Finally, we also calculated the atomic charge density values for 2-methoxy-*N*-methylcarbazole (**5**) and the corresponding values obtained are presented in Table X. As can be seen in this table, the higher atomic charge density values are localized at C-1 and C-3 owing to the introduction of a strong electron donor substituent such as the methoxy group in the *N*-methylcarbazole moiety and con-

Table IX

Static Charge Distribution for N-Benzoylcarbazole (4) [a]

Compounds	1-C 12-C	2-C 13-C	3-C 14-C	4-C 15-C	5-C 16-C	6-C	7-C	8-C	9 (NH)
4	-0.119 -0.058	-0.081 -0.108	-0.121 -0.080	-0.051 -0.106	-0.054 -0.061	-0.120	-0.085	-0.091	0.152
4a	-0.079 -0.061	-0.088 -0.106	-0.141 -0.079	-0.056 -0.108	-0.048 -0.058	-0.121	-0.078	-0.119	0.154
4b	-0.105 -0.052	-0.081 -0.109	-0.143 -0.075	-0.050 -0.108	-0.054 -0.059	-0.142	-0.085	-0.078	0.148

[a] Calculations were performed using PM3 method [23].

Table X

Static Charge Distribution for 2-Methoxy-N-methylcarbazole (5) [a]

Compounds	1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
5	-0.149	0.105	-0.207	-0.011	-0.056	-0.123	-0.086	-0.105	0.163
5a	-0.173	0.104	-0.198	-0.012	-0.054	-0.122	-0.085	-0.103	0.178
5	-0.115	0.075	-0.173	-0.041	-0.048	-0.124	-0.080	-0.107	0.171
5c	-0.142	0.072	-0.165	-0.044	-0.046	-0.123	-0.078	-0.105	0.183
5d	-0.114	0.075	-0.173	-0.041	-0.048	-0.124	-0.080	-0.107	0.171
5e	-0.142	0.072	-0.164	-0.044	-0.046	-0.123	-0.078	-0.105	0.183

[a] Calculations were performed using PM3 method [23].

sequently, a modification of the electrophilic substitution pattern in the chlorination reaction of **5** would be expected. By analyzing our experimental results presented in Table V, when we use one equivalent of N-chlorobenzotriazole 1-chloro-2-methoxy- **5a** and 3-chloro-2-methoxy-N-methylcarbazole (**5b**) are formed as the main products. When two equivalents of N-chlorobenzotriazole were used 3,6-dichloro-2-methoxy-N-methylcarbazole (**5c**) is formed as the main product together with significant amounts of **5a** and **5b**. Also, when three equivalents of N-chlorobenzotriazole were used 1,3,6-trichloro-2-methoxy-N-methylcarbazole (**5d**) was formed in a fairly good yield together with significant amounts of compounds **5c** and **5e**. According to our experimental results the electrophilic substitution pattern was similar to that observed for the N-alkyl- and N-acylcarbazoles selected in this work and these results are again in agreement with the results predicted by semiempirical calculations (see Table X). It is interesting to mention that 1,3-dichloro-2-methoxy-N-methylcarbazole would be formed from **5a** as a dichlorinated product together with compound **5c** as can be seen from the higher charge density value calculated for C-3 of compound **5a**. Nevertheless, under our experimental conditions using two equivalents of N-chlorobenzotriazole the dichlorinated compound mentioned above was not formed.

To gain further insight into the reactivity of chlorocarbazoles in the ground and electronic excited state a series of studies on different carbazole derivatives are in progress in our laboratory.

EXPERIMENTAL

Thin layer chromatography (tlc) analysis was performed with aluminium silica gel sheets (0.2 layer thickness, silica-gel 60 F254). Gas chromatography (gc) analysis was conducted with a HP-17 column (crosslinked 50% phenylmethylsilicone; 10 m x 2.0 µm film, megabore column) and an Ultra-2 column (crosslinked 5% phenylsilicone; 25 m x 0.2 mm x 0.33 µm; capillary column).

Mass spectra (ms) were obtained under electron impact (70 eV). The ratio m/z and the relative intensities are reported. Gas chromatography-mass spectra (gc-ms) analysis was conducted with the Ultra-2 column. Products were isolated by column chromatography using silica gel 200-400 mesh 60Å and hexane and hexane-ethyl acetate mixtures were used as eluent. Melting points are uncorrected. The [1]H-nmr and ^{13}C-nmr spectra were determined in deuteriochloroform at 200 MHz. Chemical shifts are reported in ppm values, using tetramethylsilane as internal standard. The ^{13}C-nmr assignements were confirmed by using the DEPT pulse sequence.

Dichloromethane, chloroform, acetonitrile, hexane, ethyl acetate and other reagents used were analytical grade. Solvents

were freshly distilled and dried before using. *N*-Methylcarbazole, 2-hydroxycarbazole and *N*-phenylcarbazole were purchased from Aldrich. *N*-Acetylcarbazole and *N*-benzoylcarbazole were prepared according to the procedure that we previously described [11-13]. 2-Methoxy-*N*-methylcarbazole was prepared according to the procedure described by Oikawa [24], and obtained as white needles after crystallized from ethanol, mp 97° (lit 97-98° [24]) The spectroscopic data (^{1}H-nmr and ^{13}C-nmr) of the 2-methoxy-*N*-methylcarbazole obtained were similar to those reported in the literature [24].

General Procedure for the Chlorination Reaction of *N*-substituted Carbazole Derivatives 1-5 with *N*-Chlorobenzotriazole.

Chlorination Reaction of *N*-Methylcarbazole (**1**).

All of these reactions were carried out under a normal atmosphere (air). To a stirred solution of *N*-methylcarbazole (**1**) (2.76 mmoles) in chloroform (15 ml), whether or not containing silica gel (6 g) depending on the chlorination method used, a solution of *N*-chlorobenzotriazole (2.76 mmoles to 11.04 mmoles depending on the stoichiometry used) in chloroform (10 ml) was added dropwise. The reaction was stirred for an appropriate time in the absence of light, at room temperature until the tlc and gc indicated that it was completed. The reaction mixture was then filtered and the silica gel washed with chloroform (3 x 15 ml). The combined extracts were washed with water and the organic layer was dried over potassium carbonate, filtered and evaporated *in vacuo* to give a greenish solid residue. The residue was separated by column chromatography (silica gel, hexane-ethyl acetate) to give 1-chloro-*N*-methylcarbazole (**1a**), 3-chloro-*N*-methylcarbazole (**1b**), 3,6-dichloro-*N*-methylcarbazole (**1c**), 1,6-dichloro-*N*-methylcarbazole (**1d**), 1,3,6-trichloro-*N*-methylcarbazole (**1e**) and 1,3,6,8-tetrachloro-*N*-methylcarbazole (**1f**). According to the experimental conditions used the percentage yield of the products obtained are diferent and they are presented in Table I.

1-Chloro-*N*-methylcarbazole (**1a**).

This compound was obtained as white needles (ethanol), mp 70-71° (lit 70-71° [22]); ^{1}H-nmr (deuteriochloroform): δ 8.04 (d, 1H, 4-H, J = 7.7 Hz), 7.99 (dd, 1H, 5-H, J = 1.9, 7 Hz), 7.40 (m, 3H, 2-, 6- and 7-H, J = 2.0, 7.5 Hz), 7.25 (m, 2H, 3- and 8-H, J = 2.0, 7.5 Hz), 4.25 ppm (s, 3H, NCH$_3$); ms: m/z 217 (37.3), 215 (M$^+$, 100), 200 (7.1), 179 (10.7), 165 (4.3), 164 (10.7), 152 (17.1), 150 (6.0).

Anal. Calcd. for C$_{13}$H$_{10}$NCl: C, 72.39; H, 4.67; N, 6.49; Cl, 16.44. Found: C, 72.30; H, 4.69; N, 6.47; Cl, 16.48.

3-Chloro-*N*-methylcarbazole (**1b**).

This compound was obtained as white crystals (hexane), mp 40-42° (lit 38-40° [22]); ^{1}H-nmr (deuteriochloroform): δ 8.00 (d, 1H, 4-H, J = 1.4 Hz), 7.92 (dd, 1H, 5-H, J = 1.5, 7.7 Hz), 7.45 (m, 3H, 2-, 6- and 7-H, J = 1.5, 8 Hz), 7.13 (dt, 2H, 8- and 1-H, J = 8 Hz), 4.22 ppm (s, 3H, NCH$_3$); ms: m/z 217 (39.3), 215 (M$^+$, 100), 200 (11.0), 180 (12.4), 179 (7.9), 164 (11.3), 152 (16.7), 151 (9.2), 150 (4.8), 137 (3.5).

Anal. Calcd. for C$_{13}$H$_{10}$NCl: C, 72.39; H, 4.67; N, 6.49; Cl, 16.44. Found: C, 72.37; H, 4.68; N, 6.50; Cl, 16.42.

1,6-Dichloro-*N*-methylcarbazole (**1c**).

This compound was obtained as white needles (ethanol), mp 54-55°; ^{1}H-nmr (deuteriochloroform): δ 8.05 (d, 1H, 5-H, J =

2.1 Hz), 8.05 (d, 1H, 4-H, J = 7.69 Hz), 7.51 (dt, 1H, 2-H, J = 1.1, 7.1 Hz), 7.43 (dd, 1H, 7-H, J = 2.0, 8.74 Hz), 7.41 (d, 1H, 8-H, J = 8.37 Hz), 3.84 ppm (s, 3H, CH$_3$); ms: m/z 253 (15.2), 251 (74.2), 249 (M$^+$, 100.0), 236 (1.9), 234 (3.2), 216 (57.9), 214 (98.0), 200 (19.5), 186 (7.4), 178 (23), 164 (28.6), 152 (35.1), 149 (23.2), 138 (8.1).

Anal. Calcd. for C$_{13}$H$_9$NCl$_2$: C, 62.43; H, 3.63; N, 5.60; Cl, 28.35. Found: C, 62.44; H, 3.65; N, 5.60; Cl, 28.34.

3,6-Dichloro-*N*-methylcarbazole (**1d**).

This compound was obtained as white needles (ethanol), mp 159-160° (lit 158-159° [22]); ^{1}H-nmr (deuteriochloroform): δ 7.91 (d, 2H, 4- and 5-H, J = 1.83 Hz), 7.38 (dd, 2H, 2- and 7-H, J = 1.9, 8.69 Hz), 7.23 (d, 2H, 1- and 8-H, J = 8.80 Hz), 3.75 ppm (s, 3H, CH$_3$), ms: m/z 253 (11.7), 251 (66.2), 249 (M$^+$, 100.0), 234 (11.1), 217 (18.5), 215 (53.7), 200 (7.2), 178 (8.9), 164 (15.1), 152 (15.1), 149 (23.2), 137 (6.8).

Anal. Calcd. for C$_{13}$H$_9$NCl$_2$: C, 62.43; H, 3.63; N, 5.60; Cl, 28.35. Found: C, 62.44; H, 3.65; N, 5.60, Cl, 28.34.

1,3,6,8-Tetrachloro-*N*-methylcarbazole (**1d**).

This compound was obtained as white plates (ethanol), mp 137-139°; ^{1}H-nmr (deuteriochloroform): δ 7.77 (d, 2H, 4- and 5-H, J = 2.0 Hz), 7.41 (d, 2H, 2- and 7-H, J = 2.0 Hz), 4.46 ppm (s, 3H, CH$_3$); ms: m/z 323 (8), 321 (42), 319 (100), 317 (M$^+$, 81), 308 (4), 306 (22), 304 (56), 302 (43), 271 (1), 269 (6), 267 (10), 236 (15), 234 (3), 232 (2), 199 (25), 197 (8), 163 (4), 135 (18), 116 (29).

Anal. Calcd. for C$_{12}$H$_4$NCl$_4$: C, 49.41; H, 1.28; N, 4.43; Cl, 44.88. Found: C, 49.40; H, 1.29; N, 4.43; Cl, 44.89.

Chlorination Reaction of *N*-phenylcarbazole (**2**).

The chlorination reaction of *N*-phenylcarbazole was performed according to the general procedure described above. These reactions were conducted at 25° and at 55°. The green-yellowish solid residue was separated by column chromatography (silica-gel-hexane-ethyl acetate) to give two crystalline products **2a** and **2b**. The percentage yield of the products obtained are presented in Table II (see Results and Discussion).

3-Chloro-*N*-phenylcarbazole (**2a**).

This compound was obtained as white needles (ethanol), mp 93-94°; ^{1}H-nmr (deuteriochloroform): δ 8.04 (dd, 1H, 5-H, J = 7.0, 2.0 Hz), 7.99 (d, 1H, 4-H, J = 1.7 Hz), 7.50-7.43 (m, 3H, 2-, 6- and 7-H), 7.36 (m, 5H, 9-, 10-, 11-, 12- and 13-H), 7.28 (m, 1H, 8-H), 7.23 ppm (d, 1H, 1-H, J = 8.6 Hz); ms: m/z 279 (35.8), 277 (M$^+$, 100.0), 243 (7.6), 242 (13.8), 241 (30.2), 200 (2.4), 164 (5.1), 138 (2.5), 105 (1.3).

Anal. Calcd. for C$_{18}$H$_{12}$NCl: C, 77.84, H, 4.35; N, 5.04; Cl, 12.76. Found: C, 77.85; H, 4.33; N, 5.05; Cl, 12 77.

3,6-Dichloro-*N*-phenylcarbazole (**2b**).

This compound was obtained as white needles (ethanol), mp 156-158°; ^{1}H-nmr (deuteriochloroform): δ 8.00 (d, 2H, 4- and 5-H, J = 1.7 Hz), 7.28 (d. 2H, 1- and 8-H, J = 7.1 Hz), 7.55 (dd, 2H, 2- and 7-H, J = 7.1, 1.7 Hz), 7.35 ppm (m, 5H, 9-, 10-, 11-, 12- and 13-H); ms: m/z 315 (2.6), 313 (14.0), 311 (M$^+$, 21.3), 279 (35.8), 277 (100.0), 243 (7.6), 241 (30.2), 240 (8.8), 200 (2.4), 164 (5.1), 138 (2.5), 105 (2.3).

Anal. Calcd. for C$_{18}$H$_{11}$NCl$_2$: C, 69.25; H, 3.55; N, 4.49; Cl, 22.71. Found: C, 69.24; H, 3.56; N, 4.44; Cl, 22.69.

Chlorination Reaction of N-Acetylcarbazole (3).

The chlorination reaction of N-acetylcarbazole was performed according to the general procedure described above. These reactions were heated at reflux for an appropriate period of time until the tlc and gc indicated that it was completed. The green-yellowish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate) to give four crystalline products, 1-chloro-N-acetylcarbazole (**3a**), 3-chloro-N-acetylcarbazole (**3b**), 1,6-dichloro-N-acetylcarbazole (**3c**) and 3,6-dichloro-N-acetylcarbazole (**3d**). The percentage yield of the products obtained are presented in Table III (see Results and Discussion)

1-Chloro-N-acetylcarbazole (3a).

This compound was obtained as white needles (ethanol), mp 221-222°; [1]H-nmr (deuteriochloroform): δ 8.09 (d, 1H, 8-H, J = 8 Hz), 7.97 (d, 1H, 5-H, J = 8.2 Hz), 7.94 (d, 1H, 4-H, J = 8 Hz), 7.49 (d, 1H, 2-H, J = 8 Hz), 7.43 (m, 3H, 3-, 6- and 7-H, J = 2, 8 Hz), 2.84 ppm (s, 3H, CH_3); ms: m/z 275 (15.2), 273 (45.5), 245 (9.1), 243 (M^+, 27.3), 230 (12.1), 229 (33.3), 228 (45.5), 227 (100), 202 (12.1), 201 (21.2), 200 (39.4), 199 (20.8), 164 (42.2), 138 (6.1), 44 (27.3).

Anal. Calcd. for $C_{14}H_{10}NOCl$: C, 69.00; H, 4.14; N, 5.75, O, 6.57; Cl, 14.55. Found: C, 68.97; H, 4.12; N, 5.77; O, 6.54; Cl, 14.56.

3-Chloro-N-acetylcarbazole (3b).

This compound was obtained as white plates (ethanol), mp 123-125° (lit 124-125° [22]); [1]H-nmr (deuteriochloroform): δ 8.15 (d, 1H, 8-H, J = 9 Hz), 8.07 (d, 1H, 1-H, J = 8 Hz), 7.89 (d, 1H, 5-H, J = 8 Hz), 7.86 (s, 1H, 4-H), 7.49 (m, 3-H, 2-, 6- and 7-H); ^{13}C-nmr (deuteriochloroform): δ 169.7 (CO), 140 (9a-C), 138 (8a-C), 129.3 (3-C), 127.9 (2-C), 127.2 (7-C), 125.3 (4a-, 4b-C), 123.8 (6-C), 120.1 (4-C), 119.4 (5-C), 117.5 (1-C), 115.9 (8-C), 27.6 (CH_3); ms: m/z 275 (18.2), 273 (51.5), 245 (9.1), 243 (M^+, 27.3), 230 (12.1), 229 (33.3), 228 (45.5), 227 (100), 202 (12.1), 201 (21.2), 200 (39.4), 199 (20.8), 164 (42.2), 138 (6.1), 44 (27.3).

Anal. Calcd. for $C_{14}H_{10}NOCl$: C, 69.00; H, 4.14; N, 5.75; O, 6.57; Cl, 14.55. Found: C, 68.99; H, 4.15; N, 5.76; O, 6.54; Cl, 14.53.

1,6-Dichloro-N-acetylcarbazole (3c).

This compound was obtained as a white solid (ethanol), mp 175°; [1]H-nmr (deuteriochloroform): δ 8.04 (d, 1H, 8-H, J = 8.9 Hz), 7.93 (s, 1H, 5-H), 7.91 (dd, 1H, 4-H, J = 1.1, 7.8 Hz), 7.52 (dd, 1H, 2-H, J = 1.1, 7.8 Hz), 7.46 (dd, 1H, 7-H, J = 8.8), 7.37 (t, 1H, 3-H, J = 2.2, 8.8 Hz), 2.67 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{19}NOCl_2$: C, 60.46; H, 3.26; N, 5.04; O, 5.57; Cl, 25.49. Found: C, 60.47; H, 3.27; N, 5.02; O, 5.56; Cl, 25.48.

3,6-Dichloro-N-acetylcarbazole (3d).

This compound was obtained as white plates (ethanol), mp 183-185° (lit 185-186° [20]); [1]H-nmr (deuteriochloroform): δ 8.09 (d, 2H, 1-, 8-H, J = 8.9 Hz), 7.83 (d, 2H, 4-, 5-H, J = 2.2 Hz), 7.42 (dd, 2H, 2-, 7-H, J = 2.2, 8.9 Hz), 2.83 ppm (s, 3H, CH_3); ^{13}C-nmr (deuteriochloroform): δ 168.5 (CO), 140.2 (8a-, 9a-C), 129.5 (3-C), 127.9 (2-, 7-C), 126.5 (4a-, 4b-C), 119.7 (4-, 5-H), 117.2 (1-, 8-C), 27.5 ppm (CH_3); ms: m/z 281 (57.8), 277 (M^+, 100), 266 (13.8), 264 (66.1), 262 (90.8), 239 (8.9), 237

(12.8), 235 (77.1), 202 (9.2), 200 (27.5), 164 (41.3), 139 (15.6), 137 (24.7), 117 (37.6).

Anal. Calcd. for $C_{14}H_9NOCl_2$: C, 60.46, H, 3.26; N, 5.04; O, 5.57; Cl, 25.49. Found: C, 60.43; H, 3.28; N, 5.07; O, 5.56; Cl, 25.50.

Chlorination Reaction of N-Benzoylcarbazole (4).

The chlorination reaction of N-benzoylcarbazole was performed according to the general procedure described above. These reactions were heated at reflux for an appropriate period of time until the tlc and gc indicated that it was completed. The green-yellowish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate) to give two crystalline products 3-chloro-N-benzoylcarbazole (**4a**) and 3,6-dichloro-N-benzoylcarbazole (**4b**). The percentage yield of the products obtained are presented in Table IV (see Results and Discussion).

3-Chloro-N-Benzoylcarbazole (4a).

This compound was obtained as white needles after recrystallization from ethanol, mp 221-222°; [1]H-nmr (deuterichloroform): δ 7.95 (d, 1H, 4-H, J = 8 Hz), 7.89 (m, 2H, 12-, 16-H, J = 7.5 Hz), 7.53 (m, 2H, 1-, 8-H, J = 7.9 Hz), 7.31 ppm (m, 6H, 2-, 7-, 6-, 14-, 13-, 15-H); ^{13}C-nmr (deuteriochloroform): δ 169.4 (CO), 139.9 (9a-C), 137.8 (8a-C), 135.4 (11-C), 132.7 (14-C), 130.7 (3-C), 128.9 (12-, 13-, 16-, 15-C), 127.3 (2-C), 126.7 (7-C), 126.1 (4a-C), 124.9 (4b-C), 123.5 (6-C), 119.9 (4-C), 119.7 (5-C), 116.8 (1-C), 115.7 ppm (8-C); ms: m/z 307 (M^+, 4), 305 (12), 271 (3), 203 (6), 201 (18), 166 (9), 164 (4), 105 (100), 77 (43.3).

Anal. Calcd. for $C_{19}H_{12}NOCl$: C, 74.64; H, 3.96; N, 4.58; O, 5.23; Cl, 11.59. Found: C, 74.62; H, 3.92; N, 4.55; O, 5.23; Cl, 11.60.

3,6-Dichloro-N-benzoylcarbazole (4b).

This compound was obtained as white needles (ethanol), mp 236°; [1]H-nmr (deuteriochloroform): δ 7.78 (d, 2H, 4-, 5-H, J = 1.5 Hz), 7.58 (d, 2H, 12-, 16-H, J = 7.6 Hz), 7.44 (m, 3H, 15-, 14-, 13-H, J = 7.5 Hz), 7.29 (d, 2H, 1-, 8-H, J = 8.8 Hz), 7.18 ppm (dd, 2H, 7-, 2-H, J = 1.8, 6.8 Hz); ^{13}C-nmr (deuteriochloroform): δ 170.2 (CO), 137.8 (9a-, 8a-C), 135.0 (11-C), 132.8 (14-C), 130.1 (6-, 3-C), 129.0 (16-, 12-, 15-, 13-C), 127.4 (2-, 7-C), 126.2 (4a-, 4b-C), 119.8 (5-, 4-C), 116.9 ppm (8-, 1-C); ms: m/z 343 (5), 341 (4), 339 (M^+, 5), 307 (4), 305 (9), 269 (5), 238 (1), 236 (2), 234 (4), 200 (2), 198 (3), 105 (100), 77 (36).

Anal. Calcd. for $C_{19}H_{11}NOCl_2$: C, 67.08; H, 3.26; N, 4.12; O, 4.70; Cl, 20.84. Found: C, 67.05; H, 3.28; N, 4.15; O, 4.73; Cl, 20.81.

Chlorination Reaction of 2-Methoxy-N-methylcarbazole (5).

The chlorination reaction of 2-methoxy-N-methylcarbazole (**5**) was performed according to the general procedure describe above. These reactions were conducted at -18° and at 25°. The yellowish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate) to give three crystalline products 1-chloro-2-methoxy-N-methylcarbazole (**5a**), 3-chloro-2-methoxy-N-methylcarbazole (**5b**) and 3,6-dichloro-2-methoxy-N-methylcarbazole (**5c**). The percentage yield of the products obtained are presented in Table V (see Results and Discussion).

1-Chloro-2-methoxy-*N*-methylcarbazole (5a).

This compound was obtained as white needles (ethanol), mp 125-127°; ^{1}H-nmr (deuteriochloroform): δ 7.97 (d, 1H, 5-H, J = 7.7 Hz), 7.90 (d, 1H, 4-H, J = 8.5 Hz), 7.55-7.32 (m, 2H, 6- and 7-H), 7.23 (t, 1H, 8-H, J = 2, 7.7 Hz), 6.89 (d, 1H, 3-H, J = 8.5 Hz), 4.23 (s, 3H, OCH$_3$), 4.00 ppm (s, 3H, NCH$_3$); ms: m/z 247 (32.7), 245 (M$^+$, 100), 232 (16), 230 (50), 204 (17.3), 202 (58), 187 (12.3), 167 (9.5), 152 (13.8).

Anal. Calcd. for C$_{14}$H$_{12}$NOCl: C, 68.44; H, 4.92; N, 5.70; O, 6.51; Cl, 14.43. Found: C, 68.43; H, 4.94; N, 5.67; O, 6.56; Cl, 14.45.

3-Chloro-2-methoxy-*N*-methylcarbazole (5b).

This compound was obtained as white crystals (ethanol), mp 168-169°; ^{1}H-nmr (deuteriochloroform): δ 8.04 (s, 1H, 4-H), 7.96 (d, 1H, 5-H, J = 7.6 Hz), 7.55-7.30 (m, 2H, 6-, 7-H), 7.22 (t, 1H, 8-H, J = 1.8, 7.8 Hz), 6.87 (s, 1H, 1-H), 4.04 (s, 3H, OCH$_3$), 3.81 ppm (s, 3H, NCH$_3$); ms: m/z 247 (33.2), 245 (M$^+$, 100), 232 (8.8), 230 (26.1), 204 (18.5), 202 (60), 187 (8.9), 166 (8.2), 152 (10.2).

Anal. Calcd. for C$_{14}$H$_{12}$NOCl: C, 68.44; H, 4.92; N, 5.70; O, 6.51; Cl, 14.43. Found: C, 68.43; H, 4.94; N, 5.71; O, 6.49; Cl, 14.42.

3,6-Dichloro-2-methoxy-*N*-methylcarbazole (5c).

This compound was obtained as white needles (ethanol), mp 169-171°; ^{1}H-nmr (deuteriochloroform): δ 7.97 (s, 1H, 4-H), 7.88 (d, 1H, 5-H, J = 1.7 Hz), 7.36 (dd, 1H, 7-H, J = 8.73, 2.1 Hz), 7.24 (d, 1H, 8-H, J = 8.67 Hz), 6.83 (s, 1H, 1-H), 4.03 (s, 3H, OCH$_3$), 3.78 ppm (s, 3H, NCH$_3$); ms: m/z 283 (20.6), 281 (88), 279 (M$^+$, 100), 268 (6.7), 266 (39.3), 264 (61.1), 240 (8.8), 238 (50.3), 236 (74.6), 217 (6.3), 215 (18.8), 201 (16.2), 186 (9.1), 178 (5.5), 166 (14.7), 139 (29.8).

Anal. Calcd. for C$_{14}$H$_{11}$NOCl$_2$: C, 60.02, H, 3.96; N, 5.00; O, 5.71; Cl, 25.31. Found: C, 60.03; H, 3.94; N, 5.07; O, 5.71; Cl, 25.32.

1,3,6-Trichloro-2-methoxy-*N*-methylcarbazole (5d).

This compound was obtained as white needles (ethanol), mp 143-145°; ^{1}H-nmr (deuteriochloroform): δ 7.91 (s, 1H, 4-H), 7.90 (s, 1H, 5-H), 7.44 (dd, 1H, 7-H, J = 8.8, 2.1 Hz), 7.30 (d, 1H, 8-H, J = 8.9 Hz), 4.20 (s, 3H, NCH$_3$), 3.99 ppm (s, 3H, OCH$_3$); ms: m/z 319 (4), 317 (28), 315 (100), 313 (M$^+$, 85.7), 304 (2.7), 302 (16.9), 300 (59.9), 298 (53.9), 274 (19), 272 (56), 270 (61.2), 257 (14.3), 237 (7.2), 235 (10.8), 217 (15.5), 215 (47), 200 (17.7), 185 (11.6), 164 (14.8), 137 (8.4).

Anal. Calcd. for C$_{14}$H$_{10}$NOCl$_3$: C, 53.45; H, 3.20; N, 4.45; O, 5.09; Cl, 33.81. Found: C, 53.42; H, 3.22; N, 4.41; O, 5.06; Cl, 33.82.

1,3,8-Trichloro-2-methoxy-*N*-methylcarbazole (5e).

This compound was obtained as a white solid (ethanol), mp 132-134°; ^{1}H-nmr (deuteriochloroform): δ 7.89 (s, 1H, 4-H), 7.80 (dd, 1H, 5-H, J = 1.05, 7.72 Hz), 7.40 (dd, 1H, 7-H, J = 1.03, 7.73 Hz), 7.13 (t, 1H, 6-H, J = 7.72 Hz), 4.49 (s, 3H, OCH$_3$), 3.98 ppm (s, 3H, NCH$_3$); ms: m/z 319 (3.0), 317 (26.2), 315 (78.8), 313 (82.7), 304 (2), 302 (14.9), 300 (45.8), 298 (48.3), 283 (11.8), 281 (67.1), 279 (100), 268 (7.7), 266 (41.8), 264 (67.3), 238 (35.5), 236 (56.6), 221 (5.0), 200 (14.6), 186 (12.2), 164 (11.8), 140 (21.9).

Anal. Calcd. for C$_{14}$H$_{10}$NOCl$_3$: C, 53.45; H, 3.20; N, 4.45; O, 5.09; Cl, 33.81. Found: C, 53.42; H, 3.22; N, 4.41; O, 5.06; Cl, 33.82.

Chlorination Reaction of *N*-Acetylcarbazole (3) and *N*-Benzoylcarbazole (4) with *N*-Chlorosuccinimide.

According to the general procedure, a solution of *N*-acetylcarbazole (200 mg, 0.96 mmole) in chloroform (10 ml) was allowed to react with a solution of *N*-chlorosuccinimide (146.8 mg, 0.96 mmole) in chloroform (5 ml) in the presence or absence of silica-gel (2 g) depending on the chlorination method used. The greenish solid residue was separated by column chromatography to give **3a**, **3b** and **3c**. The percentage yields of the products obtained are shown in Table III.

In a similar manner as described above, a solution of *N*-benzoylcarbazole (200 mg, 0.74 mmole) in chloroform (10 ml) was allowed to react with a solution of *N*-chlorosuccinimide (113.2 mg, 0.74 mmole) in chloroform (5 ml) in the presence or absence of silica-gel (2 g) depending on the chlorination method used. The greenish solid residue was separated by column chromatography to give **4a** and **4b**. The percentage yields of the products obtained are shown in Table IV.

Calculations.

The ground-state geometry and heat of formation, static charge distribution for predicting chemical reactivity of *N*-substituted-carbazole and chlorocarbazole derivatives were calculated by using the semiempirical parametrized PM3 method as implemented in version release 4.5 of the HyperChem program [23], which has proven to be effective in studies on moleculars containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

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