On the Synthesis and Isolation of Chlorocarbazoles Obtained by Chlorination of Carbazoles

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Carbazole (**1**) undergoes electrophilic aromatic substitution with various chlorinating reagents. Although 3-chlorocarbazole (**1b**), 3,6-dichlorocarbazole (**1d**) and 1,3,6,8-tetrachlorocarbazole (**1f**) obtained by chlorination of carbazole were isolated and characterized sometime ago, 1-chlorocarbazole (**1a**), 1,6-dichlorocarbazole (**1c**) and 1,3,6-trichlorocarbazole (**1e**) had never been isolated from the reaction mixtures. The preparation and subsequent isolation and characterization of **1a**, **1b**, **1c**, **1d**, **1e** and **1f** are reported (mp, t_R, R_f, ^{1}H- and ^{13}C-nmr, ms). Physical and spectroscopic properties of **1c** are compared with those of **1b** and **1d** in order to show that the former is the major product obtained in several chlorinating processes. As chlorinating reagents, chlorine in glacial acetic acid, sulfuryl chloride, *N*-chlorosuccinimide, *N*-chlorosuccinimide-silica gel, *N*-chlorobenzotriazole, and *N*-chlorobenzotriazole-silica gel in dichloromethane and in chloroform have been used and their uses have been compared. The chlorination reaction of different carbazole derivatives such as 2-hydroxycarbazole (**2**), 2-acetoxycarbazole (**3**), 3-bromocarbazole (**4**) and 3-nitrocarbazole (**5**) was also studied and the corresponding chloro derivatives **2a**, **2b**, **2c**, **2d**, **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **4a**, **4b**, **4c**, **4d**, **5a** and **5b** are described for the first time. Semiempirical PM3 calculations have been performed in order to predict reactivity of carbazole (**1**), substituted carbazoles **2-5** and chlorocarbazoles (Scheme 1). Theoretical and experimental results are discussed briefly.

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During the course of our work concerning the photochemical behavior of aromatic nitrogen organic compounds, we examined the photochemical reactions of carbazoles [1,2], azacarbazoles [3-9] and *N*-acylcarbazoles [10-12]. We also studied the photoinduced single electron transfer processes which occur from the azacarbazoles [4-9] and carbazoles [12] (electron donor) to halomethanes (electron acceptors: dichloromethane, trichloromethane and tetrachloromethane). Owing to a non-reversible photoinduced electron transfer process [13] from carbazole (**1**) several chlorocarbazole derivatives were obtained: 1-chlorocarbazole (**1a**), 3-chlorocarbazole (**1b**), 1,6-dichlorocarbazole (**1c**), 3,6-dichlorocarbazole (**1d**), 1,3,6-trichlorocarbazole (**1e**) and 1,3,6,8-tetrachlorocarbazole (**1f**). In order to study the photochemical behaviour of these chloro derivatives and chlorocarbazoles in general we decided to prepare chlorocarbazoles by thermal methods (Scheme 1).

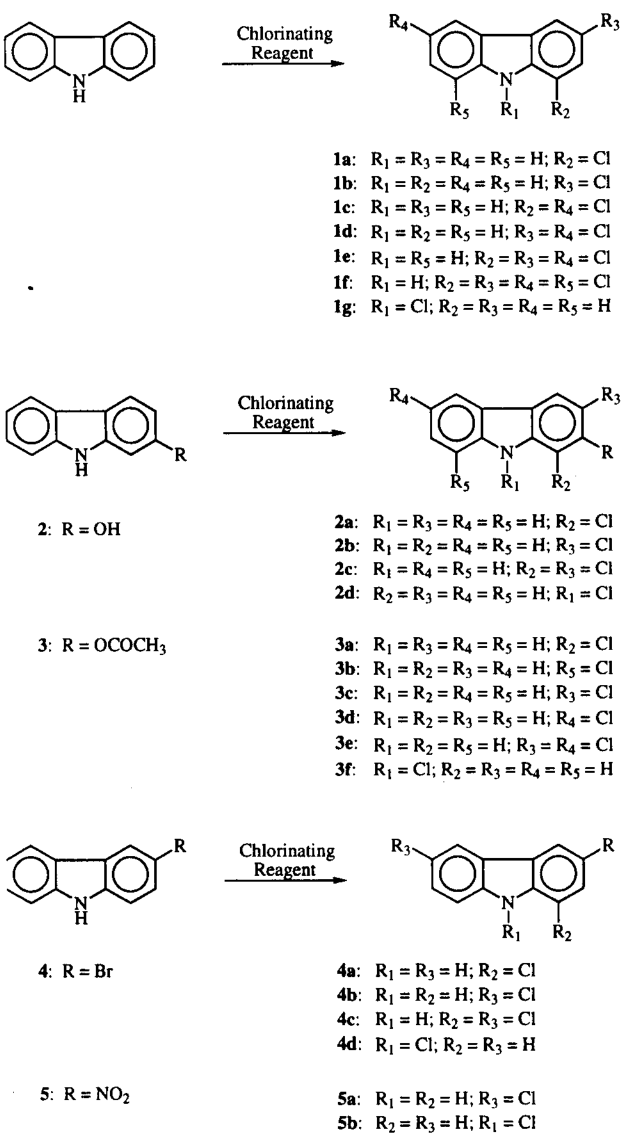
Quenching of the first excited singlet electronic state of carbazole by electron acceptors has attracted the attention of investigators. Owing to these photophysical property, polymers containing the pendant carbazolyl chromophore are good electron donors and possess outstanding electrical and photoelectrical properties [14,15]. Thus, the knowledge of the photophysical properties of chlorocarbazoles is neccesary to decide if polymers containing as pendant chlorocarbazolyl chromophores would be of use as electrical and photoelectrical conductors.

According to our knowledge, although the synthesis of some chlorocarbazoles were described some time ago [16-19] product studies (isolation and characterization) had been limited by the difficulty of separating the products formed [20-22] and in some cases it would appear that product ratios reported just reflect the ease of separation of the products. Recently, De Rosa *et al.* [20] called as "an inseparable" the mixture of carbazole and chlorocarbazoles obtained, using only ^{1}H-nmr to determine composition after *N*-methylation of the reaction mixture while not attempting the isolation of these chloro derivatives. Previously, owing to the same problem, Johnson had used isotope dilution to determine products in the reaction mixture obtained by chlorination of *N*-acetylcarbazole [22].

Traditional methods of chlorination of carbazole generally provide **1b** [16,17,22-24] and **1d** [16,17,23,24] depending on the ratio of substrate to reagent used. By polychlorination it is also possible to obtain **1e** and **1f**, but more forcing conditions are required in order to obtain higher yields giving rise to even more experimental problems which usually produce complex mixtures. Previously, **1a** and **1d** were obtained as part of a mixture in poor yields [20] but they were not characterized.

In the present paper, we describe several chloro derivatives obtained from carbazole (**1**) and for the first time chloro derivatives were obtained from substituted carbazoles such as 2-hydroxycarbazole (**2**), 2-acetoxycarbazole (**3**), 3-bromocarbazole (**4**) and 3-nitrocarbazole (**5**) (Scheme 1). Also, we describe the use of several chromatograpic methods (tlc, column chromatography, gc and gc-ms) in order i) to follow the chlorination reactions and

Scheme 1



1a: $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = Cl$
1b: $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Cl$
1c: $R_1 = R_3 = R_5 = H$; $R_2 = R_4 = Cl$
1d: $R_1 = R_2 = R_5 = H$; $R_3 = R_4 = Cl$
1e: $R_1 = R_5 = H$; $R_2 = R_3 = R_4 = Cl$
1f: $R_1 = H$; $R_2 = R_3 = R_4 = R_5 = Cl$
1g: $R_1 = Cl$; $R_2 = R_3 = R_4 = R_5 = H$

2: R = OH

2a: $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = Cl$
2b: $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Cl$
2c: $R_1 = R_4 = R_5 = H$; $R_2 = R_3 = Cl$
2d: $R_2 = R_3 = R_4 = R_5 = H$; $R_1 = Cl$

3: R = $OCOCH_3$

3a: $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = Cl$
3b: $R_1 = R_2 = R_3 = R_4 = H$; $R_5 = Cl$
3c: $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Cl$
3d: $R_1 = R_2 = R_3 = R_5 = H$; $R_4 = Cl$
3e: $R_1 = R_2 = R_5 = H$; $R_3 = R_4 = Cl$
3f: $R_1 = Cl$; $R_2 = R_3 = R_4 = R_5 = H$

4: R = Br

4a: $R_1 = R_3 = H$; $R_2 = Cl$
4b: $R_1 = R_2 = H$; $R_3 = Cl$
4c: $R_1 = H$; $R_2 = R_3 = Cl$
4d: $R_1 = Cl$; $R_2 = R_3 = H$

5: R = NO_2

5a: $R_1 = R_2 = H$; $R_3 = Cl$
5b: $R_2 = R_3 = H$; $R_1 = Cl$

to study their kinetics, ii) to determine the product yields and iii) to isolate for identification (R_f, t_R, mp, uv, ^{1}H-nmr, ^{13}C-nmr, ms) each of the chlorinated derivatives obtained. Also, we have introduced *N*-chlorosuccinimide, *N*-chlorosuccinimide-silica gel, *N*-chlorobenzotriazole and *N*-chlorobenzotriazole-silica gel as convenient new chlorinating reagents.

Quantum chemical calculation using the PM3 method have been used to obtain the geometrical feature of all the carbazoles and chlorocarbazoles (Scheme 1) used during the course of our work. The charge density values calculated for the more relevant atoms are collected in Tables III, VIII, IX, X, and XI and they are used to discuss the reactivity of carbazole.

Results and Discussion.

Chlorination of Carbazole (**1**).

In order to prepare chlorocarbazoles we decided to use first the classical methods to obtain **1b** [1,2,17,25] and **1d** [1,2,16,17,25] (Table I, methods 1, 2A and 2B) and the acid-catalyzed intermolecular rearrangement of *N*-chlorocarbazole (**1g**) [20] to obtain **1a** and **1c**. As can be seen in Table I (method 3) and in the Experimental, in our hands the latter reaction provides 62% of **1c** this value being quite different than that previously reported (3-5%) [20]. Furthermore, **1b** was detected neither by tlc nor gc or gc-ms although the same paper reports a high yield of 3-chlorocarbazole (11-51%) [20]. The quite different methods used to determine the composition of the mixtures obtained (^{1}H-nmr of the *N*-methylated reaction mixture in reference [20]; gc and gc-ms in the present paper) and modifications introduced in the experimental procedure might explain the different results obtained. Thus, our method is more convenient for high yield preparation of the dichlorocarbazole **1c**.

Chlorination of carbazole (**1**) using *N*-chlorosuccinimide and glacial acetic acid to obtain 3,6-dichlorocarbazole (**1d**) [22], provided in our hands at room temperature a poor yield of **1c** (Table I, method 4A, 7.3%), this value being raised after refluxing the reaction mixture during 6 hours (Table I, method 4B, 35%). When *N*-chlorobenzotriazole in dichloromethane was used as the reagent (Table I, method 5), a simple and quite clean synthesis of **1c** was provided (yield 71%). This results surprised us because *N*-chlorobenzotriazole in dichloromethane (**1** to *N*-chlorobenzotriazole molar ratio 1:1) had been described some time ago as an excellent method to prepare 3-chlorocarbazole (**1b**) (yield 79%) [26], characterized only by its mp and its elemental analyses [26]. As can be seen in Table I and in the Experimental R_f and t_R values for **1b** and **1c** are quite different as well as their ^{1}H-, ^{13}C-nmr and ms.

As shown in Table I (R_f and t_R values) and in the Experimental, we improved the methods to analyze the composition of the reactions mixtures obtained by chlorination of carbazole (tlc, gc and gc-ms) and the chromatographic methods to isolate and purify the chloro derivatives (silica gel sheets and columns). Thus, it was easy to control and to follow the chlorination processes.

Taking into account that *N*-bromosuccinimide-silica gel reagent had been introduced as a convenient reagent system for the bromination of carbazole [27] we decided to study the use of *N*-chlorosuccinimide and *N*-chlorosuccinimide-silica gel together with the *N*-chlorobenzotriazole and *N*-chlorobenzotriazole-silica gel systems as reagents for the chlorination of carbazoles.

Thus, carbazole in chloroform with *N*-chlorosuccinimide was treated (molar ratio 1:1) in the presence of sil-

Table I

Chlorination of Carbazole by Using Different Methods

			Method (% yield) [a]										
Products	R_f	t_R [a]	1 [b]	2A [c]	2B [c]	3 [d]	4A [e]	4B [e]	5 [f]	6A [g]	6B [g]	7 [h]	8 [i]
1f	0.85	4.43	-	-	-	-	1.0	-	-	74	94	7.0	-
1a	0.72	1.13	-	-	-	3.7	-	5.5	7.7	-	-	12	1.8
1b	0.68	2.65	-	100	-	-	-	-	-	-	-	-	37
1e	0.60	5.28	-	-	-	-	-	-	-	17	5.0	-	48
1	0.55	0.96	-	-	-	22	48	-	12	9.0	-	21	-
1c	0.47	2.36	-	-	-	62	7.3	35	71	-	-	57	-
1d	0.34	5.84	100	-	100	12	44	60	9.2	-	-	9.3	12

[a] Quantitative gc analysis (HP-17 column), t_R in minutes. [b] Chlorine in glacial acetic acid at 0° [16]. [c] Sulfuryl chloride in chloroform; carbazole to sulfuryl chloride molar ratio: method 2A (1:1) and method 2B (1:2) [1,2,17]. [d] Rearrangement of *N*-chlorocarbazole. [e] *N*-Chlorosuccinimide in glacial acetic acid; method 4A: room temperature during 18 hours; method 4B: refluxing time 6 hours. [f] *N*-Chlorobenzotriazole in dichloromethane; carbazole to *N*-chlorobenzotriazole molar ratio: (1:1), refluxing time 6 hours. [g] *N*-Chlorobenzotriazole in dichloromethane; carbazole to *N*-chlorobenzotriazole molar ratio: (1:4); method 6A: refluxing time 6 hours; method 6B: refluxing time 18 hours. [h] *N*-Chlorosuccinimide-silica gel in dichloromethane; carbazole to *N*-chlorosuccinimide molar ratio (1:1); room temperature during 19 hours. [i] *N*-Chlorosuccinimide-silica gel in dichloromethane; carbazole to *N*-chlorosuccinimide molar ratio (1:2); room temperature during 35 hours. [a-i] For more details see Experimental.

Table II

Chlorination Reaction of Carbazole (**1**) by Using *N*-Chlorobenzotriazole and *N*-Chlorosuccinimide

					Products (%) [a]				
Experiment No.	Temperature (°C)	Carbazole: *N*-chlorobenzotriazole (molar ratio)	Silica-gel (g)	Time (minutes)	**1**	**1a**	**1b**	**1c**	**1d**
N-Chlorobenzotriazole in Dichloromethane									
1	25	1:1	-	35	20	8	-	65	7
2	25	1:1	10	35	30	11	-	50	9
3	25	1:2	-	60	-	5	14	13	67
4	25	1:2	2	35	4	3	15	18	59
5	-20	1:2	-	50	4	2	14	8	70
N-Chlorobenzotriazole in Chloroform.									
6	-20	1:1	6	55	66	-	-	31	3
7	25	1:1	-	55	80	-	-	8	12
8	25	1:1	6	55	33	11	-	46	10
9	25	1:1	-	55	59	-	-	16	24
10	25	1:1	10	55	33	11	-	46	10
11	-20	1:2	-	55	-	5	21		74
N-Chlorosuccinimide in Chloroform.									
12	-20	1:1 [b]	6	65	96	-	-	4	-
13	-20	1:1 [b]	-	65	18	15	-	61	6
14	25	1:1 [b]	6	75	36	9	-	50	5
15	25	1:1 [b]	-	65	18	15	-	62	6

[a] Quantitative gc (HP-17) analysis. [b] Carbazole to *N*-chlorosuccinimide molar ratio.

ica gel both at 25° and at -20° and the yields of the products were determined by gc (Table II, experiments 12 and 14). Simultaneously, we ran some experiments with *N*-chlorosuccinimide in chloroform without silica gel (Table II, experiments 13 and 15). Besides, similar experiments were run using *N*-chlorobenzotriazole and *N*-chlorobenzotriazole-silica gel as chlorinating reagents, in dichloromethane and in chloroform, at different temperatures (-20° and 25°) with different *N*-chlorobenzotriazole to carbazole molar ratios (1:1 and 1:2), during different periods of time (Table II, experiments 1 to 11). The reactions were monitored (gc) every five minutes to obtain additional information about the rates of formation of chlorocarbazole derivatives. As shown in Table II when the carbazole to *N*-chlorobenzotriazole molar ratio is 1:1, **1b** is not detected as a stable product. 1,6-Dichlorocarbazole (**1c**) is the main product in dichloromethane solution while in chloroform solution the ratio of **1c** to **1d**, the yield is higher when the experiments were performed in the presence of silica gel. When the carbazole to *N*-chlorobenzotriazole molar ratio was 1:2 (Table II, experiments 3, 4, 5 and 11) the composition of the reaction mixture was quite different. While **1d** was always the main product, **1c** and **lb** were always detected in the reaction mixture. In contrast, Ledwith [26] reported **1d** as the only product in the reaction mixture.

When *N*-chlorosuccinimide was used as the chlorinating reagent (carbazole to *N*-chlorosuccinimide molar ratio 1:1), **1c** was again the main reaction product obtained, diminishing slightly the conversion of carbazole by the presence of silica gel in the medium (Table II, experiments 12 and 14). Under our experimental conditions the composition of the reaction mixture (Table II, experiments 1 to 15) was the same, within experimental error, at 60 minutes and at 1440 minutes, it not being necessary to set aside the reaction overnight to improve the yields. When *N*-chlorobenzotriazole was used in dichloromethane at room temperature (Table I, *N*-chlorobenzotriazole to **1** molar ratio 4:1, method 6A) carbazole was easily into **1e** (17% yield) and **1f** (74% yield). Besides, carbazole could be converted into **1f** rapidly, cleanly and selectively by refluxing the same reaction mixture during 6 hours (Table I, method 6B, 94% yield). It is interesting to mention that the yield of **1f** is higher than that previously reported by Ledwith (61% [26])

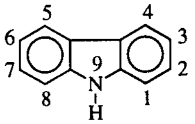
Finally, when we ran additional experiments with the *N*-chlorosuccinimide-silica gel reagent in dichloromethane at 25° (Table I, methods 7 and 8) we observed that the composition of the reaction mixtures obtained were quite different depending on the *N*-chlorosuccinimide to carbazole molar ratio used.

From the above results it is clear that *N*-chlorosuccinimide, *N*-chlorosuccinimide-silica gel, *N*-chlorobenzotriazole and *N*-chlorobenzotriazole-silica gel are particularly useful systems for selective 1,6-dichlorination of **1** as well as for a quite clean preparation of 1,3,6,8-tetrachloro derivative **1f**. These methods are not so highly selective but produce useful yields of **1a** and **1e**. Furthermore, in our hands the acid-catalyzed intermolecular rearrangement of *N*-chlorocarbazole (**1g**) proved to be a useful method to obtain 1,6-dichlorocarbazole (**1c**) in high yield. As can be seen in the Experimental, the ^{1}H-nmr and ^{13}C-nmr measured in dimethyl sulfoxide-d$_6$ for **1c** are completely different than the corresponding nmr spectra for **1d**. Compounds **1c** and **1e** are characterized for the first time in the present work. It is interesting to mention that the *N*-chlorocarbazole (**1g**) obtained by reaction of **1** with sodium hypochlorite was characterized by tlc and by ultra-violet spectroscopy which showed an hypsochromic shift characteristic of *N*-substitution with an electron withdrawing group.

As known, the high reactivity of the aromatic ring of carbazole in electrophilic substitution makes it highly probable that these reactions reflect the proven Cl+ activity of *N*-chlorobenzotriazole and *N*-chlorosuccinimide [28]. The fact that the substitution pattern observed by using *N*-chlorobenzotriazole and *N*-chlórosuccinimide (*N*-chlorosuccinimide: carbazole and *N*-chlorobenzotriazole:carbazole molar ratio 1:1, Tables I and II) is similar to that which we obtained by acid-catalyzed rearrangement of *N*-chlorocarbazole (**1g**) (Table I, method 3) suggests that an intermediate that resembling *N*-chlorocarbazole might occur during the former chlorination processes. From this unstable *N*-chlorocarbazole-like intermediate, 1,6-dichlorocarbazole (**1c**) could be easily formed in the reaction medium. Unfortunately, we could not detect the *N*-chlorocarbazole intermediate during the chlorination reation of carbazole with *N*-chlorosuccinimide or *N*-chlorobenzotriazole because of the high halogenation capability of both in homogeneous organic media, even at -18°. Experiments at lower temperature were not run because of the low solubility of carbazole in chloroform or dichloromethane. In contrast, the low chlorination capability of the chlorine cation (Cl+) generated in the heterogeneous aqueous media during the halogenation of the carbazole with sodium hypochlorite would account for the greater stability of the *N*-chlorocarbazole. A further piece of evidence in favor of the above rationalization was provided by the net atomic charge values calculated by using the semiempirical PM3 method, as implemented in the version of the HyperChem program [29], to obtain the optimized geometry of carbazoles and chloro derivatives. As can be seen in Table III Cl+ can react with **1** and carbazole anion (**1**(-)) to yield **1a** and **1b**. As the charge on C-3 is higher than on C-1 the latter would be the main product. According to our experimental results with *N*-chlorobenzotriazole and *N*-chlorosuccinimide to carbazole molar ratio 1:1, **1c** is preferentially formed. This selective and high yield formation of **1c** can be explained by taking into account that the *N*-chlorocarbazole-like intermediate by an intramolecular rearrangement would yield preferentially **1a**. While this intramolecular rearrangement takes place a structure that resembles the carbazolonium anion occurs (**1**(-), Table III). This virtual anion intermediate of low half life, would react faster than carbazole with Cl+, not only with Cl+ present in the solvent cage but also with those diffusing in the solution toward the [*N*-chlorocarbazole = carbazole anion + chlo-

Table III

Static Charge Distribution for Carbazole Compounds [a]



	Atom number								
Compounds	1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
1	-0.107	-0.082	-0.126	-0.049					0.194
1(-)	-0.138	-0.119	-0.222	-0.047					-0.298
1(.)	-0.004	-0.021	-0.014	-0.013					-0.301
1(+.)	0.023	-0.102	0.016	-0.023					0.588
1(+)	0.172	-0.164	0.078	-0.057					0.343
1g	-0.081	-0.087	-0.110	-0.057					0.087
1gH(+)	-0.001	-0.080	-0.017	-0.042					0.118
1a	-0.133	-0.082	-0.116	-0.049	-0.047	-0.126	-0.070	-0.106	0.209
1b	-0.095	-0.084	-0.146	-0.050	-0.046	0.125	-0.079	-0.107	0.208
1c	-0.134	-0.079	-0.115	-0.046	-0.048	-0.146	-0.081	-0.094	0.214
1d	-0.095	-0.081	-0.146	-0.048					0.204
1e	-0.125	-0.083	-0.139	-0.049	-0.046	-0.147	-0.079	-0.093	0.219
1f	-0.125	-0.081	-0.139	-0.046					0.237

[a] Calculations were performed using PM3 method [29].

rine cation = 1-chlorocarbazole] system within its half life. This would be the main mechanism when the carbazole to *N*-chlorosuccinimide (and *N*-chlorobenzotriazole) molar ratio is 1:1. Simultaneously, taking into account that charge distributions are frequently used for interpreting and predicting chemical reactivity and that the static charge distribution should indicate sites of kinetic attack by incoming reagents, **1** and the primary chloro derivatives formed can react with Cl+, by means of the well known electrophilic substitution, to yield **1b**, **1d**, **1e** and **1f** depending upon the final reaction scheme obtained on the carbazole to Cl+ molar ratio. The charge values calculated by PM3 method for **1a**, **1b**, **1c**, **1d**, **1e** and **1f** would explain the substitution pattern experimentally obtained (Table III). Thus, it seems certain that electrophilic attack of carbazole under a wide variety of conditions occurs preferentially at the carbon atoms with charge values higher than -0.93. Besides the calculated values for carbazolyl radical (**1**(.)), carbazolonium cation (**1**(+)) and carbazole radical cation (**1**(+.)) (Table III) suggest that they would not react with Cl+ to yield selectively 1,6-dichlorocarbazole (**1c**). Similar conclusions are obtained taking into account the values calculated for *N*-chlorocarbazole (**1g**) and protonated *N*-chlorocarbazole (**1gH**+) (Table III).

Chlorination of Substituted Carbazoles **2-5**.

In order to shed some light on the mechanism of the chlorination reaction of carbazole we decided to apply the same chlorinating reagents to substituted carbazoles whose reactivity was modified by the introduction of different substituents in one of the benzene rings of the carbazole moiety. The compounds selected for this study were 2-hydroxycarbazole (**2**), 2-acetoxycarbazole (**3**), 3-bromocarbazole (**4**) and 3-nitrocarbazole (**5**) (see Scheme 1).

Chlorination of 2-Hydroxycarbazole (**2**).

When **2** reacted with *N*-chlorobenzotriazole in a molar ratio (1:1) at room temperature according to the general procedure described in the Experimental, we obtained in a simple and clean synthesis 3-chloro-2-hydroxycarbazole (**2b**) in 45% yield. When **2** to the *N*-chlorobenzotriazole molar ratio was (1:2) the composition of the reaction mixture was quite different after the same reaction time. In this case the reaction was not selective and 1-chloro-2-hydroxycarbazole (**2a**), 3-chloro-2-hydroxycarbazole (**2b**) and 1,3-dichloro-2-hydroxycarbazole (**2c**) were obtained in 12, 16 and 29% yields, respectively. When this reaction was conducted at 55° we obtained **2c** as the main product (69% yield) together with a significant amount of **2b** (15% yield) (Table IV).

In order to obtain additional information about the rates of formation of the chloro-2-hydroxycarbazole derivatives, these experiments were monitored by gas chromatography each for five minutes. As can be seen in Figure 1, **2** was rapidly consumed to give the monochloro-2-

Table IV

Chlorination Reaction of 2-Hydroxycarbazole (**2**) by Using *N*-Chlorobenzotriazole and Sodium Hypochlorite

Temperature (°C)	**2**:*N*-Chlorobenzotriazole (molar:ratio)	Time (minutes)	Product Yield (%) [a]			
			2	**2a**	**2b**	**2c**
-18	1:1	45	37	18	49	-
25	1:1	19	35	20	45	-
55	1:1	60	44	13	16	28
25	1:2	60	57	12	16	29
55	1:2	60	16	-	15	69
50	[b]	10	15	14	16	30

[a] Quantitative gc (HP-17) analysis. [b] Chlorination reaction of 2-hydroxycarbazole by using sodium hypochlorite.

hydroxycarbazoles **2a** and **2b** as the primary products, which in turn gave the dichloro-2-hydroxycarbazole **2c** as the main product.

Chlorination of 2-Acetoxycarbazole (**3**).

Simultaneously, we carried out the chlorination reaction of 2-acetoxycarbazole (**3**) with one equivalent of *N*-chlorobenzotriazole according to the general procedure described in the Experimental at -18° and at 25° during nineteen minutes. In both cases we obtained four chlorinated products: 1-chloro-2-acetoxycarbazole (**3a**), 8-chloro-2-acetoxycarbazole (**3b**), 3-chloro-2-acetoxycarbazole (**3c**) and 6-chloro-2-acetoxycarbazole (**3d**), **3c** and **3d** being the main products. The percentage yields are shown in Table V. When the **3** to *N*-chlorobenzotriazole molar ratio is 1:2 this reaction had the same kinetic profile as shown in Figure 1 for **2** and carbazole **3** was rapidly consumed to give 3-chloro-2-acetoxycarbazole (**3c**) as the primary product, which in turn gave the 3,6-dichloro-2-acetoxycarbazole (**3b**). Thus under these experimental conditions the main product obtained was the 3,6-dichloro derivative **3e** in a fairly good yield (see TableV).

Chlorination of 3-Bromocarbazole (**4**).

The chlorination reaction of 3-bromocarbazole (**4**) was carried out in chloroform in the presence of one equivalent of *N*-chlorobenzotriazole at room temperature during sixty minutes. This reaction was not selective and three

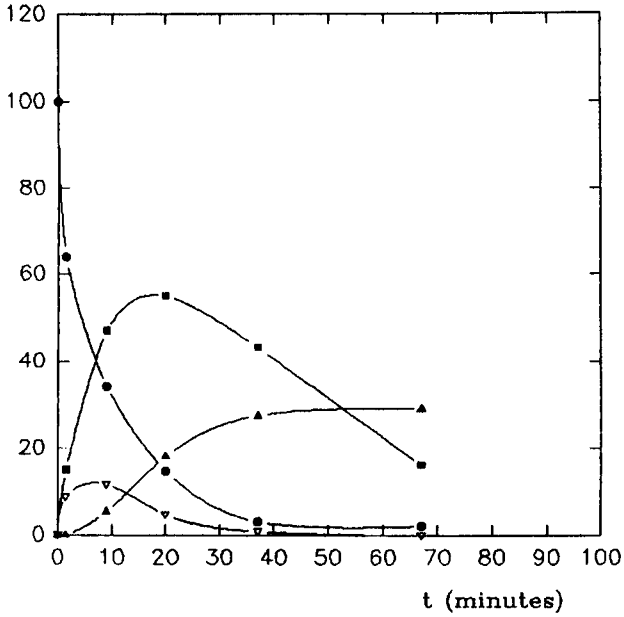


Figure 1. Kinetic plot for the chlorination reaction of 2-hydroxycarbazole (**2**) with *N*-chlorobenzotrizole. **2** to *N*-chlorobenzotriazole molar ratio (1:2).

(•) **2**

(▽) **2a**

(■) **2b**

(▲) **2c**

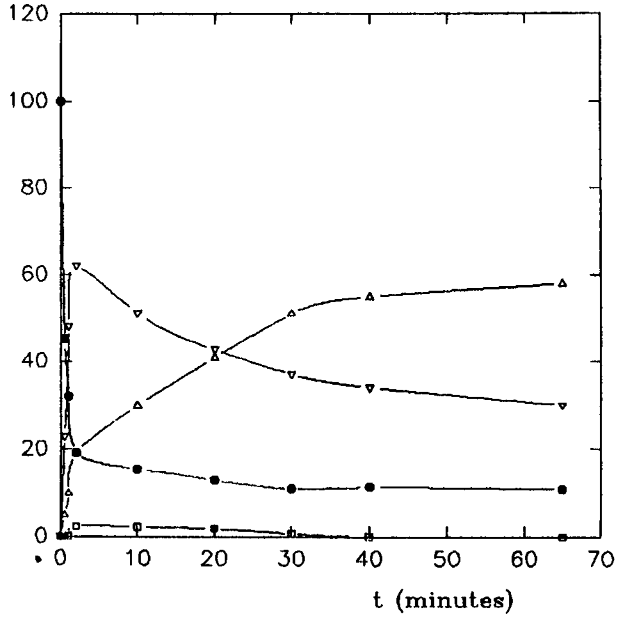


Figure 2. Kinetic plot for the chlorination reaction of 3-bromocarbazole (**4**) with *N*-chlorobenzotriazole. **4** to *N*-chlorobenzotriazole molar ratio (1:2).

(•) **4**

(□) **4a**

(▽) **4b**

(△) **4c**

Table V

Chlorination Reaction of 2-Acetoxycarbazole (**3**) by Using *N*-Chlorobenzotriazole and Sodium Hypochlorite

Temperature (°C)	**3**:*N*-Chlorobenzotriazole (molar:ratio)	Time (minutes)	Products Yield (%) [a] **3**	**3a**	**3b**	**3c**	**3d**	**3e**
-18	(1:1)	35	29	2.1	4.1	26	39	-
25	(1:1)	20	10	4.2	8.1	30	44	-
25	(1:2)	10	4.7	1.3	2.9	11	16	57
50	[b]	10	25	2.8	4.5	28	41	6.9

[a] Quantitative gc (HP-17) analysis. [b] Chlorination reaction of 2-acetoxycarbazole by using sodium hypochlorite.

products were obtained: 1-chloro-3-bromocarbazole (**4a**), 6-chloro-3-bromocarbazole (**4b**) and 1,6-dichloro-3-bromocarbazole (**4c**) (see Table VI). By analyzing the rate profiles shown in Figure 2 we can conclude that **4a** and **4b** are the primary products which in turn gave **4c** as the main product. Even working at low temperature (till -18°) we could not provide a selective formation of the monochloro derivatives **4a** and **4b**. When the chlorination reaction of **4** with two equivalents of *N*-chlorobenzotriazole was run at room temperature the reaction mixture was quite different. In this case we obtained in a fairly selective route to **4c** (Table VI).

Table VI

Chlorination Reaction of 3-Bromocarbazole (**4**) by Using *N*-Chlorobenzotriazole and Sodium Hypochlorite

Temperature (°C)	**4**:*N*-Chlorobenzotriazole (molar:ratio)	Time (minutes)	Product Yield (%) [a] **4**	**4a**	**4b**	**4c**
-18	(1:1)	85	35	17	40	8.2
25	(1:1)	60	36	14	37	12
25	(1:2)	30	12	0.2	30	58
50	[b]	15	41	12	30	19

[a] Quantitative gc (HP-17) analysis. [b] Chlorination reaction of 3-bromocarbazole by using sodium hypochlorite.

Chlorination of 3-Nitrocarbazole (**5**).

We also studied the chlorination reaction of 3-nitrocarbazole (**5**) by using one equivalent of *N*-chlorobenzotriazole at -18° and at room temperature during sixty minutes. In both experiments 6-chloro-3-nitrocarbazole (**5a**) was obtained as the sole product in 87% yield. When the chlorination reaction was carried out with two equivalents of *N*-chlorobenzotriazole at room temperature, again the only product detected in the reaction mixture was **5a** in 87% yield (Table VII).

This particular behaviour shown by **5** in comparison with other substituted carbazoles studied in the present work may be rationalized taking into account its low reactivity towards the chlorine cation because of the presence of a withdrawing substituent in the carbazole moiety.

Table VII

Chlorination Reaction of 3-Nitrocarbazole (**5**) by Using *N*-Chlorobenzotriazole and Sodium Hypochlorite

Temperature (°C)	**4**:*N*-Chlorobenzotriazole (molar:ratio)	Time (minutes)	Product Yield (%) [a] **5**	**5a**
-18	(1:1)	60	18	82
25	(1:1)	60	13	87
25	(1:2)	30	13	87
50	[b]			

[a] Quantitative gc (HP-17) analysis. [b] Chlorination reaction of 3-nitrocarbazole by using sodium hypochlorite.

It is noteworthy to mention that during the chlorination reaction of **5** we could detect 3-nitro-*N*-chlorocarbazole (**5b**) as a reaction intermediate which rearranged to **5a**.

Chlorination of **2-5** with Sodium Hypochlorite.

Simultaneously, we prepared the *N*-chloro derivatives of **2**, **3**, **4** and **5** by reaction of the corresponding carbazoles with sodium hypochlorite (see Scheme 1, compounds **2d**, **3f**, **4d** and **5b** and the Experimental). Solutions of these *N*-chlorocarbazoles were iodometrically characterized. The carbazoles **2d**, **3f** and **4d** were only characterized by tlc because removal of the solvent under reduced pressure at room temperature gave a short-lived solid that decomposed with the evolution of hydrogen chloride except in the case of 3-nitro-*N*-chlorocarbazole (**5b**). This latter compound was stable both in chloroform solution and in the solid state without the occurance of any rearrangement during the removal of the solvent. Thus, we could record the ultraviolet spectra of the **5b** in acetonitrile solution. The hypsochromic shift of the lower energy band was observed by comparison with the ultraviolet spectra of 3-nitrocarbazole.

The acid-catalyzed intermolecular rearrangement of the *N*-chlorocarbazoles **2d**, **3f**, **4d** and **5b** were conducted according to the general method described in the Experimental and the products obtained and their yields are shown in Tables IV, V, VI and VII, respectively.

By comparison of the chlorinated products obtained by acid-catalyzed rearrangement of the *N*-chlorocarbazole derivatives with those obtained by using *N*-chlorobenzotriazole as a chlorinating reagent, we can conclude that intermediates that resemble *N*-chlorocarbazoles might occur during the latter chlorination processes.

Reactivity of Carbazoles **2-5**. Semiempirical Calculations.

The substitution patterns observed by using *N*-chlorobenzotriazole and sodium hypochlorite with carbazoles **2**, **3**, **4** and **5** were predicted using the net atomic charge values calculated by PM3 [29].

As can be seen in Table VIII, carbazole **2** has the higher density charge value localized at C-1 and C-3 and it was expected that the incoming chlorine cation (Cl+) would preferentially attack these positions. In agreement with this fact when the **2** to *N*-chlorobenzotriazole molar ratio was (1:1) working at -18° and 25°, 1-chloro- **2a** and 3-chloro-2-hydroxycarbazole (**2b**) were obtained as the primary products (Table IV). Then, these primary monochloro derivatives reacted with chlorine cation to yield 1,3-dichlorocarbazole **2c**. The atomic charge values calculated (PM3) for **2a** and **2b** also, explains the substitution pattern experimentally obtained (Table IV).

In Table VIII are shown the charge density values calculated for the *N*-chlorocarbazole **2d**. The suggested reaction intermediate is that in which again the highest negative charge density values are localized at C-1 and C-3. When the thermal intramolecular rearrangement of **2d** took place we obtained **2a** and **2b** as the principal products together with **2c**. The experimental substitution pattern obtained for this rearrangement agrees with results predicted by semiempirical calculations.

As can be seen in Table IX, the pattern distribution of the atomic static charge values of 2-acetoxycarbazole (**3**) is different than that observed for 2-hydroxycarbazole at 1-C and 3-C. Thus the monochloro substitution at 1-C, 3-C and at 6-C, 8-C are equally probable in 2-acetoxycarbazole (**3**) while in 2-hydroxycarbazole the substitution at 1-C and 3-C are more probable than that at 3-C and 6-C. As a consequence, five mono-chloro derivatives have been obtained from **3** chlorinated at l-C, 3-C, 6-C and 8-C (Scheme 1, compounds **3a** to **3e**) while only two monochloro derivatives from **2** (Scheme l, compounds **2a** and **2b**) chlorinated at 1-C and 3-C respectively, have been obtained. The experimental results obtained for the chlorination reaction of **3** with one or two equivalents of *N*-chlorobenzotriazole again are in agreement with the theoretical results obtained analyzing the atomic static charge calculated by semiempirical methods (see Table V).

We also calculated the charge density values for 3-bromocarbazole (**4**). The values obtained are shown in Table X and as it can be seen the highest negative charge density values are localized at C-l, C-6 and C-8. Under our experimental conditions 3-bromo-1-chloro- **4a** and 3-bromo-6-chlorocarbazole (**4b**) were formed as primary products. Also, in Table X are presented the charge density values calculated for the monochlorocarbazole derivatives **4a** and **4b** showing that the preferential position to be attact by a second chlorine cation would be the C-6 for **4a** and the C-1 for **4b**. Although, the charge density value at C-8 is significant in **4** we have not obtained any chloro derivative with a substituent at this position. According to our results the only dichlorocarbazole derivative obtained is 3-bromo-1,6-dichlorocarbazole **4c**. Besides, in Table X are shown the charge density values calculated for the *N*-chlorocarbazole **4d**, and again they are of use to predict the chlorinating substitution pattern observed (Table VI).

Table VIII

Static Charge Distribution for 2-Hydroxycarbazole (2) [a]

Compound	Atom number								
	1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
2	-0.156	+0.121	-0.219	-0.005	-0.056	-0.123	-0.086	-0.104	+0.194
2a	-0.187	+0.124	-0.212	-0.004	-0.053	-0.122	-0.084	-0.103	+0.211
2b	-0.150	+0.130	-0.243	-0.004	-0.053	-0.122	-0.083	-0.104	+0.199
2c	-0.184	+0.133	-0.238	-0.003	-0.051	-0.121	-0.081	-0.102	+0.216
2d	-0.126	+0.117	-0.208	-0.012	-0.063	-0.107	-0.091	-0.078	+0.084

[a] Calculations were performed using PM3 method [29].

Table IX

Static Charge Distribution for 2-Acetoxycarbazole (3) [a]

Compound	Atom number 1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
3	-0.120	+0.060	-0.151	-0.033	-0.048	-0.123	-0.079	-0.105	+0.200
3a	-0.157	+0.064	-0.145	-0.033	-0.046	-0.123	-0.077	-0.104	+0.212
3b	-0.119	+0.062	-0.151	-0.030	-0.048	-0.113	-0.079	-0.133	+0.213
3c	-0.111	+0.063	-0.178	-0.038	-0.046	-0.123	-0.076	-0.105	+0.201
3d	-0.120	+0.063	-0.151	-0.029	-0.050	-0.145	-0.081	-0.092	+0.203
3e	-0.111	+0.066	-0.178	-0.034	-0.047	-0.146	-0.079	-0.092	+0.206
3f	-0.095	+0.055	-0.135	-0.042	-0.055	-0.109	-0.084	-0.190	+0.082

[a] Calculations were performed using PM3 method [29].

Table X

Static Charge Distribution for 3-Bromocarbazole (4) [a]

Compound	Atom number 1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
4	-0.102	-0.064	-0.131	-0.029	-0.046	-0.125	-0.078	-0.107	+0.200
4a	-0.132	-0.064	-0.126	-0.028	-0.044	-0.124	-0.076	-0.105	+0.215
4b	-0.101	-0.061	-0.133	-0.025	-0.047	-0.146	-0.081	-0.094	+0.205
4c	-0.114	-0.070	-0.114	-0.037	-0.054	-0.135	-0.084	-0.069	+0.091
4d	-0.076	-0.069	-0.120	-0.038	-0.053	-0.109	-0.084	-0.081	+0.086

[a] Calculations were performed using PM3 method [29].

Table XI

Static Charge Distribution for 3-Nitrocarbazole (5) [a]

Compound	Atom number 1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9 (NH)
5	-0.137	+0.010	-0.447	+0.056	-0.045	-0.116	-0.076	-0.101	+0.222
5a	-0.136	+0.012	-0.445	+0.058	-0.048	-0.142	-0.080	-0.088	+0.227
5b	-0.111	+0.006	-0.426	+0.038	-0.049	-0.105	-0.080	-0.079	+0.085
5(-)	-0.175	-0.007	-0.581	+0.091	-0.067	-0.177	-0.124	-0.115	-0.254

[a] Calculations were performed using PM3 method [29].

Finally, we also calculated the atomic charge density values for 3-nitrocarbazole (**5**). As can be seen in Table XI, the higher negative atomic charge density values are localized at C-1, C-6 and C-8. It is noteworthy to notice that under our experimental conditions the only chlorinated product obtained was the 6-chloro derivative **5a** and neither 1-chloro-3-nitrocarbazole nor 1,6-dichloro-3-nitrocarbazole was obtained, even though two equivalents of *N*-chlorobenzotriazole were used (Table VII). Taking into account the atomic charge values calculated for the 3-nitrocarbazolonium anion (**5**(-)) (Table XI) a higher anionic character of the reaction intermediate would explain the results obtained.

To gain further insight into the mechanism of the above processes a series of experiments 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) . The data described in Table I are the Retention Factors (R_f). Gas chromatography (gc) analysis was conducted with a HP-17 column (Crosslinked 50% Phenyl Methyl Silicone; 10 m x 0.53 mm x 2.0 µm film; Magabor column) and an Ultra 2 column (Crosslinked 5% Phenyl Silicone; 25 m x 0.2 mm x 0.33

µm; Capillary column). The gc data described are the Retention times (t_R) obtained with the HP-17 column (Table I). Mass spectra (ms) were obtained under electron impact (70 eV). The ratios 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 preparative thick layer chromatography and column chromatography which was carried out using silica gel 200-400 mesh 60A and hexane and hexane-ethyl acetate as eluent. Melting points are uncorrected. The ^{1}H- and ^{13}C-nmr spectra were run in deuteriochloroform and dimethyl sulfoxide-d_6 at 200 MHz. Chemical shifts are reported in ppm values, using tetramethylsilane as internal standard. ^{13}C-nmr assignments were confirmed by using DEPT pulse sequence.

Dichloromethane, chloroform, acetic acid, methanol, hexane, ethyl acetate and other reagents used were analytical grade. Solvents were freshly distilled and dried before using. Carbazole and *N*-chlorosuccinimide were purchased from Aldrich. *N*-Chlorobenzotriazole, prepared by the method of Rees and Storr, gave needles from dichloromethane-petroleum ether, mp 105-106° [30]. 2-Hydroxycarbazole was purchased from Aldrich and was recrystallized from ethanol before use. 2-Acetoxycarbazole [31], 3-bromocarbazole [32] and 3-nitrocarbazole [33] were prepared according to the procedures described in the literature.

Chlorination Reaction of Carbazole (**1**).

To a stirred solution of carbazole (**1**) (543 mg, 3.25 mmoles) in dichloromethane (50 ml) whether containing silica gel (6 g) or not depending on the chlorination method used, a solution of *N*-chlorobenzotriazole (3.25 to 13.5 mmoles depending on the stoichiometry used) in dichloromethane (50 ml) was added dropwise. The reaction was stirred for an appropriate time in the absence of light at room temperature (or refluxing) until the tlc and gc indicated that it was complete. All of these reactions were carried out under a normal (air) atmosphere.The reaction mixture was then filtered and the silica-gel washed with dichloromethane (3 x 15 ml). The combined extracts were washed with water (100 ml) and the organic layer was dried over potassium carbonate, filtered and evaporated *in vacuo* to give a brownish solid residue. The residue was separated by column chromatography (silica gel-hexane-ethyl acetate mixtures) to give **1a**, **1b**, **1c**, **1d**, **1e** and **1f**. According to the experimental conditions used the percentage yield of the products obtained are different as can be seen in Table II. This set of reactions were performed in chloroform.

1-Chlorocarbazole (**1a**).

This compound was obtained as white needles (hexane), mp 106-107°; ^{1}H-nmr (deuteriochloroform): δ 8.25 (s, 1H, NH), 8.04 (d, 1H, 5-H, J = 8 Hz), 7.95 (d, 1H, 4-H, J = 8 Hz),7.42 (m, 3H, 2-, 6-, and 7-H, J = 2, 8 Hz), 7.20 ppm (m, 2H, 3- and 8-H, J = 2, 8 Hz); ^{13}C-nmr (deuteriochloroform) [34]: δ 139.3, 126.6, 125.1, 125.0, 122.4, 120.8, 120.7, 120.2, 120.1, 118.7, 116.5, 111.0 ppm; ms: m/z 203 (32), 201 (M$^+$, 100), 167 (6), 166 (34), 164 (25), 140 (7), 139 (15), 138 (11), 137 (6), 102 (4), 100 (12) 83 (6).

3-Chlorocarbazole (**1b**).

This compound was obtained as white needles (hexane), mp 198-199° ([26] 201.5°); ^{1}H-nmr (deuteriochloroform): [1,2] δ 8.21 (s, 1H, NH), 7.95 (s, 1H, 4-H), 7.85 (d, 1H, 5-H, J = 8 Hz), 7.36 (m, 3H, 2-, 6- and 7-H, J = 2, 8 Hz), 7.19 (d, 1H, 8-H, J = 8 Hz), 7.05 ppm (d, 1H, 1-H, J = 8 Hz); ^{13}C-nmr (dimethyl sulfoxide-d_6): [25,34] δ 126.2, 125.6, 123.4, 122.9, 122.8, 120.4, 120.3, 120.2, 119.8, 117.9, 113.0, 110.7 ppm; ms: m/z 204 (4), 203 (33), 202 (13), 201 (M$^+$, 100), 167 (6), 166 (40), 165 (6), 140 (12), 139 (16), 138 (6), 113 (4), 101 (9).

1,6-Dichlorocarbazole (**1c**).

This compound was obtained as white plates (hexane-ethyl acetate), mp 201-202°; ^{1}H-nmr (dimethyl sulfoxide-d_6): δ 11.37 (s, 1H, NH), 8.19 (s, 1H, 5-H), 8.13 (d, 1H, 4-H), 7.45 (m, 3H, 2-, 3- and 7-H, J = 2, 8 Hz), 7.15 ppm (d, 1H, 8-H, J = 8 Hz); ^{1}H-nmr (deuteriochloroform): δ 9.27 (s, 1H, NH), 7.95 (d, 1H, 4-H, J = 6.5 Hz), 7.94 (s, 1H, 5-H), 7.35 (m, 3H, 2-, 3- and 7-H, J = 3.3, 6.5 Hz), 7.12 ppm (d, 1H, 8-H, 6.5 Hz) (It is interesting to point out that in deuteriochloroform 4-H and 5-H signals are so close that they appear similar to a singlet but in dimethyl sulfoxide-d_6 the 4-H doublet and the 5-H singlet are clearly observed); ^{13}C-nmr (dimethyl sulfoxide-d_6): δ 140.4, 138.2, 126.3, 125.3, 123.7, 122.9, 121.6, 120.6, 119.7, 118.9, 112.3, 111.2 ppm; ms: m/z 240 (16), 238 (18), 236 (M$^+$, 21), 203 (44), 202 (29), 201 (100), 167 (33), 166 (54).

Anal. Calcd. for $C_{12}H_7NCl_2$: C, 61.05; H, 2.99; N, 5.93; Cl, 30.03. Found: C, 60.94; H, 3.05; N, 5.90; Cl, 30.09.

3,6-Dichlorocarbazole (**1d**).

This compound was obtained as white plates (hexane-ethyl acetate), mp 209-211° ([26] 212°); ^{1}H-nmr (deuteriochloroform): [1,2] δ 8.06 (s, 1H, NH), 7.96 (d, 2H, 4- and 5-H, J = 1.5 Hz), 7.38 (dd, 2H, 2- and 7-H, J = 1.5, 8.6 Hz), 7.33 ppm (d, 2H, 1- and 8-H, J = 8.6 Hz); ^{13}C-nmr (dimethyl sulfoxide-d_6): [25] δ 138.5, 125.9, 123.0, 122.6, 120.1, 112.5 ppm; ms: m/z 240 (2), 238 (18), 236 (M$^+$, 100), 203 (5), 202 (30), 201 (16), 167 (1), 166 (4), 165 (27), 164 (55), 163 (6), 140 (1), 139 (6), 113 (6), 88 (4), 87 (7).

1,3,6-Trichlorocarbazole (**1e**).

This compound was obtained as a white solid (hexane), mp 141-142°; ^{1}H-nmr (deuteriochloroform): δ 8.12 (s, 1H, NH), 7.81 (d, 1H, 5-H, J = 2 Hz), 7.70 (d, 1H, 4-H, J = 1.5 Hz), 7.45 (t, 1H, 7-H, J = 2, 8.6 Hz), 7.41 (d, 1H, 2-H, J = 1.5 Hz), 7.35 (d, 1H, 8-H, J = 8.6 Hz); ^{13}C-nmr (dimethyl sulfoxide-d_6): δ 138.9, 135.8, 126.9, 124.9, 124.1, 123.9, 123.2, 122.9, 120.7, 119.4, 116.0, 113.2 ppm; ms: m/z 275 (5), 274 (5), 273 (37), 272 (17), 271 (99), 270 (17), 269 (M$^+$, 100), 237 (5), 236 (24), 235 (8), 234 (38), 200 (10), 198 (26), 164 (12), 163 (6), 137 (6), 135 (18), 117 (17), 116 (19), 99 (18), 87 (11).

Anal. Calcd. for $C_{12}H_6NCl_3$: C, 53.27; H, 2.24; N, 5.18; Cl, 39.31. Found: C, 53.17; H, 2.26; N, 5.08; Cl, 39.01.

1,3,6,8-Tetrachlorocarbazole (**1f**).

This compound was obtained as a white solid (hexane), mp 211-212° ([26] 222-224°); ^{1}H-nmr (dimethylsulfoxide-d_6): δ 11.9 (s, 1H, NH), 8.17 (d, 2H, 4- and 5-H, J = 1.5 Hz), 7.50 ppm (d, 2H, 2- and 7-H, J = 1.5 Hz); ^{13}C-nmr (dimethyl sulfoxide-d_6): δ 136.1, 125.9, 124.4, 124.1, 119.5, 116.8 ppm; ms: m/z 309 (8), 308 (6), 307 (42), 306 (14), 305 (100), 304 (14), 303 (M$^+$, 81), 272 (6), 268 (19), 266 (22), 237 (1), 236 (3), 235 (6), 234 (16), 233 (10), 232 (23), 200 (4), 198 (12), 163 (4), 162 (12), 135 (17), 116 (29), 86 (14), 85 (23), 73 (10).

Anal. Calcd. for $C_{12}H_5NCl_4$: C, 47.26; H, 1.65; N, 4.59; Cl, 46.50. Found: C, 47.10; H, 1.57; N, 4.67; Cl, 46.35.

General Procedure for the Chlorination Reaction of Carbazoles **2**-**5** with *N*-Chlorobenzotriazole.

To a stirred solution of 2-hydroxycarbazole (**2**) (503 mg, 2.75 mmoles) in chloroform (15 ml) a solution of *N*-chlorobenzotriazole (2.75 to 5.40 mmole 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 controled temperature: -18°, 25° and 55° until gc indicated that it was completed. The workup was conducted in a similar manner as described above. The brown solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate mixtures) to give **2a**, **2b** and **2c**. The percentage yield of the products obtained are presented in Table IV (see Result and Discussion).

1-Chloro-2-hydroxycarbazole (**2a**).

This compound was obtained as white needles (hexane), mp 173-175°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 11.2 (s, 1H, NH), 10.1 (s, 1H, OH), 7.96 (d, 1H, 5-H, J = 7.7 Hz), 7.83 (d, 1H, 4-H, J = 8.4 Hz), 7.48 (d, 1-H, 6-H, J = 7.9 Hz), 7.30 (t, 1H, 7-H, J = 2, 7.7 Hz), 7.13 (t, 1H, 8-H, J = 2, 7.7 Hz), 6.85 ppm (d, 1H, 3-H, J = 8.4 Hz); ms: m/z 219 (33.4), 217 (M$^+$, 100), 182 (7.7), 154 (15.1), 153 (27), 128 (5), 127 (11), 126 (16).

Anal. Calcd. for $C_{12}H_6NOCl$: C, 66.22; H, 3.70; N, 6.44, Cl, 16.29. Found: C, 66.02; H, 3.85; N, 6.60; Cl, 16.07.

3-Chloro-2-hydroxycarbazole (**2b**).

This compound was obtained as white crystals (hexane), mp 203-205°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 11.03 (s, 1H, NH), 10.06 (s, 1H, OH), 8.06 (s, 1H, 4-H), 7.97 (d, 1H, 5-H, J = 7.7 Hz), 7.38 (d, 1H, 6-H, J = 2.0, 7.7 Hz), 7.27 (t, 1H, 7-H, J = 2.0, 7.7 Hz), 7.08 (t, 1H, 8-H, J = 1.9, 7.5 Hz), 7.05 ppm (s, 1H, 1-H); ms: m/z 219 (19.1), 217 (M$^+$, 62.1), 183 (5.7), 155 (2.2), 154 (11.3), 153 (15.2).

Anal. Calcd. for $C_{12}H_8NOCl$: C, 66.22; H, 3.70; N, 6.44; Cl, 16.29. Found: C, 66.12; H, 3.95; N, 6.38; Cl, 16.15.

1,3-Dichloro-2-hydroxycarbazole (**2c**).

This compound was obtained as white needles (hexane), mp 190°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 11.4 (s, 1H, NH), 10.5 (s, 1H, OH), 8.14 (s, 1H, 4-H), 8.04 (d, 1H, 5-H, J = 8.0 Hz), 7.46 (d, 1H, 6-H, J = 2, 8.0 Hz), 7.35 (t, 1H, 7-H, J = 1.5, 7.4 Hz), 7.15 ppm (t, 1H, 8-H, J = 1.5, 7.4 Hz); ms: m/z 255 (12.4), 253 (69.1),251 ($M^{+\bullet}$, 100); 216 (8.5); 189 (9.1); 187 (24.2); 153 (6.8); 152 (20.9); 126 (15); 125 (25.8).

Anal. Calcd. for $C_{12}H_7NOCl_2$: C, 57.17; H, 2.80; N, 5.56; Cl, 28.13. Found: C, 57.05; H, 2.79; N, 5.46; Cl, 28.12.

Chlorination Reaction of 2-Acetoxycarbazole (**3**).

The chlorination reaction of 2-acetoxycarbazole was performed according to the general procedure described above. These reactions were conducted at -18° and at room temperature. The brownish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate) to give four crystalline products **3a**, **3b**, **3c**, **3d** and **3e**. The percentage yield of the products obtained are presented in Table V (see Results and Discussion).

2-Acetoxy-1-chlorocarbazole (**3a**).

This compound was obtained as white needles (hexane) mp 120-122°; ^{1}H-nmr (deuteriochloroform): δ 8.28 (s, 1H, NH), 7.91 (d, 1H, 5-H, J = 7.7 Hz), 7.80 (d, 1H, 4-H, J = 8.2 Hz), 7.39-7.37 (m, 2H, 6- and 7-H), 7.20 (dd, 1H, 8-H, J = 1.3 and 7.7 Hz), 6.93 (d, 1H, 3-H, J = 8.2), 2.36 ppm (s, 3H, CH_3); ms: m/z 261 (5.8), 259 (M$^+$, 17.3), 219 (33.9), 217 (100), 188 (10.5), 153 (15.1) 126 (10.2).

Anal. Calcd. for $C_{14}H_{10}NO_2Cl$: C, 64.75; H, 3.88; N, 5.39; Cl, 13.65. Found: C, 64.77; H, 3.86; N, 5.73; Cl, 13.88.

2-Acetoxy-8-chlorocarbazole (**3b**).

This compound was obtained as white crystals (hexane) mp 129-131°; ^{1}H-nmr (deuteriochloroform): δ 8.29 (s, 1H, NH), 7.79 (d, 1H, 4-H, J = 8.4 Hz), 7.76 (d, 1H, 5-H, J = 7.6 Hz), 7.34-7.31 (m, 2H, 6- and 7-H), 7.10 (d, 1H, 1-H, J = 1.6 Hz), 6.88 (dd, 1H, 3-H, J = 1.6, 8.4 Hz), 2.32 ppm (s, 3H, CH_3); ms: m/z 261 (1.7), 259 (M$^+$, 5), 219 (10.3), 217 (30.4), 188 (3.2), 182 (3), 161 (9.2), 161 (9.2), 152 (4.8).

Anal. Calcd. for $C_{14}H_{10}NO_2Cl$: C, 64.75; H, 3.88; N, 5.38; Cl, 13.65. Found: C, 64.76; H, 3.85; N, 5.39, Cl, 13.68.

2-Acetoxy-3-chlorocarbazole (**3c**).

This compound was obtained as white needles (hexane) mp 164-166°; ^{1}H-nmr (deuteriochloroform): δ 8.17 (s, 1H, NH), 7.65 (d, 1H, 5-H, J = 8.1 Hz), 7.58 (s, 1H, 4-H), 7.33-7.28 (m, 2H, 6- and 7-H, J = 2, 8.5 Hz), 7.19 (dd, 1H, 8-H, J = 2, 8.5 Hz), 6.94 (s, 1H, 1-H) and 2.39 ppm (s, 3H, CH_3); ms: m/z 261 (3.5), 259 (M$^+$, 10.6), 219 (22.1), 217 (67.3), 183 (100), 154 (25.4), 126 (21.9).

Anal. Calcd. for $C_{14}H_{10}NO_2Cl$: C, 64.75; H, 3.88, N, 5.39; Cl, 13.65. Found: C, 63.99, H, 3.89; N, 5.35; Cl, 13.68.

2-Acetoxy-6-chlorocarbazole (**3d**).

This compound was obtained as a white solid (hexane) mp 182-183°; ^{1}H-nmr (deuteriochloroform): δ 8.05 (s, 1H, NH), 7.82 (s, 1H, 5-H), 7.80 (d, 1H, 4-H, J = 8.5 Hz), 7.28 (dd, 1H, 7-H, J = 2, 8.6 Hz), 7.19 (d, 1H, 8-H, J = 8.6 Hz), 7.05 (d, 1H, 1-H, J = 1.8 Hz), 6.86 (dd, 1H, 3-H, J = 1.8, 8.5 Hz), 2.31 ppm (s, 3H, CH_3); ms: m/z 261 (5), 259 (M$^+$, 14.3), 219 (33.9), 217 (100), 188 (7.1), 182 (11.9), 154 (13.6), 126 (9.4).

Anal. Calcd. for $C_{14}H_{10}NO_2Cl$: C, 64.75; H, 3.88; N, 5.39; Cl, 13.65. Found: C, 64.72; H, 3.85; N, 5.36; Cl, 13.69.

2-Acetoxy-3,6-dichlorocarbazole (**3e**).

This compound was obtained as white crystals (hexane-ethyl acetate) mp 203-204°; ^{1}H-nmr (deuteriochloroform): δ 8.29 (s, 1H, NH), 7.64 (d, 1H, 5-H, J = 1.5 Hz), 7.54 (s, 1H, 4-H), 7.36 (dd, 1H, 7-H, J = 1.5, 8.5 Hz), 7.24 (d, 1H, 8-H, J = 8.5 Hz), 6.99 (s, 1H, 1-H), 2.45 ppm (s, 3H, CH_3); ms: m/z 293 (M$^+$, 2.1), 283 (3.4), 281 (12.8), 253 (15.6), 219 (34.3), 217 (100), 200 (4.4), 188 (6), 182 (9), 164 (4), 154 (13), 153 (17.3), 126 (11.8).

Anal. Calcd. for $C_{14}H_9NO_2Cl_2$: C, 57.34; H, 3.10; N, 4.78; Cl, 23.87. Found: C, 57.32; H, 3.14; N, 4.93; Cl, 23.98.

Chlorination Reaction of 3-Bromocarbazole (**4**).

The chlorination reaction of 3-bromocarbazole was performed according to the general procedure described above. These reactions were conducted at -18° and at room temperature. The yellowish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate) to give three crystalline products **4a**, **4b** and **4c**. The percentage yield of the products obtained are presented in Table VI (see Results and Discussion).

3-Bromo-1-chlorocarbazole (**4a**).

This compound was obtained as white needles (hexane-ethyl acetate) mp 132-134°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 11.7 (s, 1H, NH), 8.38 (s, 1H, 4-H), 8.13 (d, 1H, 5-H, J = 7.7 Hz), 7.53 (s, 1H, 2-H), 7.46-7.60 (m, 2H, 6- and 7-H, J = 1.2, 7.8 Hz), 7.16 ppm (dt, 1H, 8-H, J = 7.8 Hz); ms: m/z 283 (25.7), 281 (M$^+$, 100), 279 (80.5), 237 (7.4), 235 (11.7), 201 (13.9), 200 (39.7), 175 (5.3), 173 (12.2), 165 (21.8), 164 (48.2), 149 (17.5).

Anal. Calcd. for $C_{12}H_7NClBr$: C, 51.62; H, 2.53, N, 5.02; Cl, 12.54; Br, 28.29. Found: C, 51.57; H, 2.57; N, 5.15; Cl, 12.44; Br, 28.27.

3-Bromo-6-chlorocarbazole (**4b**).

This compound was obtained as a white solid (hexane-ethyl acetate) mp 208-209°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 11.6 (s, 1H, NH), 8.28 (s, 1H, 5-H), 8.41 (s, 1H, 4-H), 7.54-7.39 ppm (m, 4-H, 1-, 2-, 7- and 8-H); ms: m/z 283 (26.9), 281 (M$^+$, 100), 279 (87.9), 246 (7.8), 244 (8.3), 202 (16.2), 200 (52.6), 174 (5.6), 173 (16.2), 165 (20.2), 164 (37), 139 (14.0).

Anal. Calcd. for $C_{12}H_7NClBr$: C, 51.62; H, 2.53; N, 5.02; Cl, 12.54; Br, 28.29. Found: C, 51.53; H, 2.60; N, 5.15; Cl, 12.39; Br, 28.33.

3-Bromo-1,6-dichlorocarbazole (**4c**).

This compound was obtained as yellow pale plates (hexane-ethyl acetate) mp 145-146°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 11.9 (s, 1H, NH), 8.45 (d, 1H, 5-H, J = 2.4, 8.0 Hz), 8.32 (d, 1H, 4-H, J = 1.4 Hz), 7.70 (d, 1H, 2-H, J = 1.4 Hz), 7.52 (dd, 1H, 7-H, J = 2.4, 8.0 Hz), 7.52 ppm (d, 1H, 8-H, J = 8.0 Hz); ms: m/z 317 (42.2), 315 (M$^+$, 100), 313 (55.9), 283 (10.9), 281 (43.6), 279 (36.0), 253 (14.5), 251 (22), 236 (14.3), 234 (21.1), 219 (6.3), 217 (17.9), 202 (5.6), 200 (21.7), 165 (11.4), 164 (32.7), 139 (15.8).

Anal. Calcd. for $C_{12}H_6NCl_2Br$: C, 46.02; H, 1.93; N, 4.48; Cl, 22.35; Br, 25.22. Found: C, 46.04; H, 1.90; N, 4.50; Cl, 22.40; Br, 25.24.

Chlorination Reaction of 3-Nitrocarbazole (**5**).

The chlorination reaction of 3-nitrocarbazole was performed according to the general procedure described above. These reactions were conducted at -18° and at room temperature. The yellowish solid residue was separated by column chromatography (silica gel-hexane-ethyl acetate) to give a crystalline product **5a**. The percentage yield of the products obtained are presented in Table VI (see Results and Discussion).

6-Chloro-3-nitrocarbazole (**5a**).

This compound was obtained as yellow needles (hexane-ethyl acetate) mp 303-305°; ^{1}H-nmr (dimethyl sulfoxide-d$_6$): δ 12.2 (s, 1H, NH), 9.22 (d, 1H, 4-H, J = 2.3 Hz), 8.5 (d, 1H, 5-H, J = 1.9 Hz), 8.30 (dd, 1H, 2-H, J = 2.3, 9.1 Hz), 7.63 (d, 1H, 1-H, J = 9.1 Hz), 7.60 (d, 1H, 8-H, J = 8.7 Hz), 7.50 ppm (dd, 1H, 7-H, J = 2.0, 8.6 Hz); ms: m/z 248 (31.9), 246 (M$^+$,100), 218 (8.4), 216 (26.1), 202 (18.7), 200 (56.3), 188 (11.4), 173 (24.3), 164 (32.2), 138 (13.4).

Anal. Calcd. for $C_{12}H_7N_2O_2Cl$: C, 58.53; H, 2.87; N, 11.38; Cl, 14.21. Found: C, 58.56; H, 2.89; N, 11.40; Cl, 14.19.

N-Chlorination of Carbazole (**1**) and Carbazoles **2-5**. Thermal Rearrangement of the *N*-Chlorocarbazoles.

To a vigorously stirred solution containing 1.716 g (10.3 mmoles) of carbazole (**1**) in 150 ml of dichloromethane were added 25 ml of *ca.* 1.73 M solution of freshly prepared sodium hypochlorite and 25 ml of water. The mixture was stirred for 48 hours. The organic layer was separated, dried over potassium carbonate, filtered and analyzed iodometrically. In the solutions obtained a 100% of pure product (*N*-chlorocarbazole) [20] was observed and carbazole was not detected (tlc). To 150 ml of a solution of *N*-chlorocarbazole (2.070 g, 10.3 mmoles) was added 50 ml of methanol and the solvent was removed by evaporation *in vacuo* (39 mm Hg, 30°). The tlc and gc of the brown solid residue dissolved in anhydrous methanol (10 ml) indicated essentially four products and the product mixture was then separated by column chromatography (silica gel-ethyl acetate) to give **1a**, **1c** and **1d**. The percentage yield of the products obtained are shown in Table I.

The *N*-chlorination of carbazole derivatives **2**, **3** and **5** were performed according to the general procedure described above. The organic solutions of these *N*-chlorocarbazole derivatives were analyzed iodometrically and all solutions contain 100% of a pure product (*N*-chlorocarbazole derivative) characterized by tlc.

The ultra-violet spectra of a diluted acetonitrile solution of 3-nitro-*N*-chlorocarbazole (**5b**) was recorded. By comparison with the ultra-violet spectra of a solution of 3-nitrocarbazole (**5**) recorded under similar experimental conditions, an hypsochromic shift was observed. The results obtained follow: **5**, uv: λ max 280 nm (ε 25,000), λ max 306 (ε 15,000), λ max 364 (ε 11,000); **5b**, uv: λ max 276 nm (ε 48,000), λ max 304 (ε 26,000), λ max 354 (ε 20,000).

The thermal rearrangement of the *N*-chlorocarbazole derivatives of **2**, **3** and **5** were performed according to the general procedure described above. The solid mixtures obtained as residues were separated by column chromatography (silica gel-hexane-ethyl acetate). The percentage yield of the products isolated are presented in Tables IV, V, VI and VII.

Chlorination Reaction of Carbazole (**1**) with *N*-Chlorosuccinimide.

In a similar manner as described for the chlorination of carbazole with *N*-chlorobenzotriazole, 543 mg (3.25 mmoles) of **1** in chloroform solution was allowed to react with 3.25 to 13.9 mmoles of *N*-chlorosuccinimide depending on the stoichiometry used in the presence or absence of silica gel (2 g) depending on the chlorination method used. The progress of the reaction was monitored by tlc and gc and the workup was conducted according to the general procedure of the chlorination reaction. The greenish solid obtained was separated by column chromatography (silica-gel-hexane ethyl acetate) to give **1a**, **1b**, **1c**, **1d**, **1e** and **1f**. The percentage yield of the products obtained are presented in Tables I and II.

Chlorination Reaction of Carbazole (**1**) with *N*-Chlorosuccinimide in Glacial Acetic Acid.

To a stirred solution of **1** (3.25 mmoles) in glacial acetic acid (60 ml), *N*-chlorosuccinimide (3.25 mmoles) was added. The reaction mixture was kept in the dark and continuously stirred at an appropriate temperature until tlc and gc indicated that it was complete. Then water was added (30 ml) and powdered sodium bicarbonate while the mixture was cooled in an ice bath with vigorous stirring. After *p*H 7 was reached, dichloromethane (20 ml) was added, the organic layer was filtered, washed twice with an equal volume of water, and dried with anhydrous calcium dichloride. The solvent was removed by evaporation *in vacuo* to give a brown solid residue. The brown residue obtained was separated by column chromatography to give **1a**, **1c**, **1d** and **1f**. The percentage yield of the products obtained are presented in Table I.

Chlorination Reaction of Carbazole (1) with Chlorine in Glacial Acetic Acid.

This reaction was conducted according to the method described by Graebe [16]. The reaction mixtures were analyzed by tlc, gc and gc-ms. After passing the reaction mixture through aluminum oxide, the filtered solution obtained was evaporated *in vacuo* to yield a white residue, which was recrystallized from ethanol to give **1d** in 100% yield (see Table I).

Chlorination Reaction of Carbazole (1) with Sulfuryl Chloride.

This reaction was conducted according to the method described by Mazzara [17]. The progress of the reaction mixture was analyzed by tlc, gc and gc-ms. The reaction mixture was concentrated, passed through silica gel, and the filtered solution was evaporated *in vacuo* providing a white solid. When a molar ratio of carbazole to sulfuryl chloride (1:1) was used, the white solid recrystallized from ethanol affored white needles of **1b** in a 100% yield. When the molar ratio of carbazole to sulfuryl chloride was (1:2) the white solid recrystallized from aqueous ethanol afforded white plates of **1d** in a 100% yield (see Table I).

Calculations.

The ground-state geometry and heat of formation, static charge distribution for predicting chemical reactivity of carbazoles **1-5**, chlorocarbazoles and possible reaction intermediates were calculated by using the semiempirical parametrized PM3 method as implemented in version of the HyperChem program [29], which has proven to be effective in studies on molecular containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

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