A study of Substituent Effect on ^1H and ^{13}C nmr Spectra of *N*- and C-Substituted Carbazoles

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^1H and ^{13}C nmr spectra of several *N*- and C-substituted carbazoles (Series 1, 2, 3 and 4) were measured. Correlations between chemical shifts and substituent constants show that these parameters describe properly the substituent effect on the nmr phenomena. Atomic charge densities for carbazoles of Series 1, 2, 3 and 4 were calculated by using the semi empirical PM3 method. These values also show a linear correlation with the ^{13}C chemical shifts. The synthesis of several carbazole derivatives **1a** - **1g**, **2a** - **2g**, **3a - 3j** and **4a – 4g** have been carried out according to literature procedures. The carbazoles **3i**, **3j** and **4c** have been synthesized and fully characterized for the first time.

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Nuclear magnetic resonance parameters, mainly chemical shifts, have been widely applied as a probe of electronic substituent effects [1-10]. The utility of this technique is based on the linear dependence between the measured substituent induced chemical shifts and the calculated electron densities. To determine the extent of transmission of these effects in aromatic derivatives, ^{13}C is the most frequently used nuclei [1]. It shows a large chemical shift range for a series of substituents attached to the ring. This also refers to heteroaromatic compounds, such as carbazole and carbazole derivatives, whose chemical shifts are sensitive to the electronic character of the interacting substituents expressed by the substituent constants [2]. This analysis shows quantitatively the inductive, resonance and/or p-polarization effect on the electron distribution of aromatic compounds in their ground state [1].

Although, ^1H and ^{13}C nmr spectra are included in previously reported papers as an ordinary tool for the characterization of carbazole derivatives [11-22] only members of the Series 1 showed in Scheme I were submitted to a transmition substituent effects on ^{13}C nmr study [16,17a].

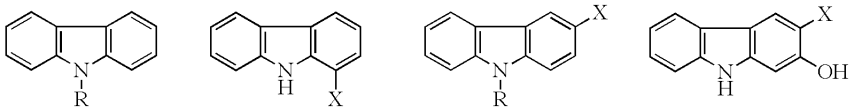
Besides, in previous papers we also reported ^1H and ^{13}C nmr data for some C-substituted [23-26] and *N*-substituted carbazoles [27,28] without any substituent chemical shift analysis.

Taking into account that no similar studies have been carried out for these carbazoles altogether we now describe the ^1H and ^{13}C nmr spectra of several *N*-substituted carbazoles (Series 1), C-substituted carbazoles (Series 2 and 3) and 2-hydroxy-C-substituted carbazoles (Series 4) shown in Scheme I with a view to understanding the factors underlying the transmission of substituent effects in these systems. These and earlier data are analysed by means of substituent chemical shift correlations.

Furthermore, in order to accomplish this spectroscopic analysis we synthesized several carbazole derivatives (**1a** - **1g**, **2a** - **2g**, **3a - 3j** and **4a – 4g**) according to optimised literature procedures and they have been fully characterized by means of physical and spectroscopic methods. Compounds **3i**, **3j** and **4c** were synthesized for the first time through one-pot chemical reactions under mild experimental conditions and full characterized. Compound **2g** was fully characterized by spectroscopic methods for the first time.

The numbering system of carbazole and its derivatives used for the present work is shown in 1.

Scheme I



Series 1 R		Series 2 X		Series 3 R; X		Series 4 X	
1a	H	**2a**	H	**3a**	R: H; X: H	**4a**	H
1b	Me	**2b**	Cl	**3b**	R: H; X: Cl	**4b**	Cl
1c	CH_2Ph	**2c**	Br	**3c**	R: H; X: Br	**4c**	Br
1d	Ph	**2d**	I	**3d**	R: H; X: I	**4d**	COMe
1e	COMe	**2e**	COPh	**3e**	R: H; X: COPh	**4e**	COPh
1f	COPh	**2f**	NO_2	**3f**	R: H; X: NO_2	**4f**	SO_2Ph
1g	$COCF_3$	**2g**	NH_2	**3g**	R: Et; X: NH_2	**4g**	NO_2
1h	CHO			**3h**	R: H; X: NHCOMe		
				3i	R: H; X: CH_2COCH_3		
				3j	R: H; X: NMe_2		

Results and Discussion.

Synthesis of Carbazole Derivatives.

In order to study the substituent effect on ^{1}H and ^{13}C nmr spectra of *N*- and C-substituted carbazoles and to increase the number of substituents attached to the carbazole moiety, we decided to carry out the synthesis of some new carbazole derivatives.

In previous studies we have reported the synthesis of several C- and *N*-substituted carbazoles shown in Scheme I that have been fully characterized by means of physical and spectroscopic methods.

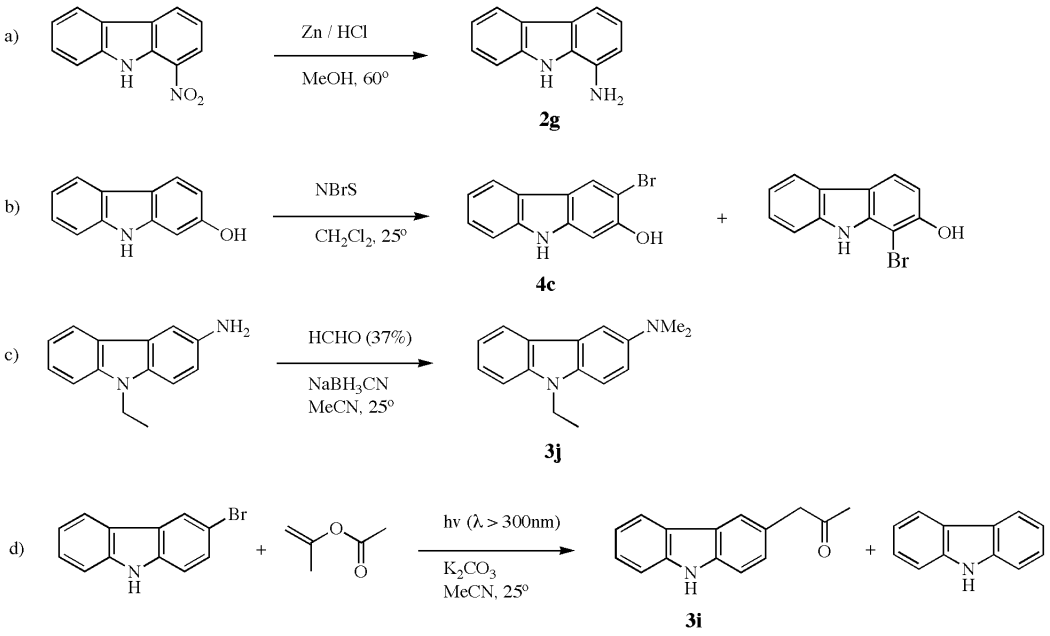
Whitner [29] has reported for the first time the synthesis of 1-aminocarbazole (**2g**) and it has been accomplished by heating an ethanolic solution of 1-nitrocarbazole in the presence of potassium hydroxide and zinc dust. The chemical yield obtained was not higher than 60% and the reduced product was only characterized by its melting point. In the same report, the author mentioned that the amino compound could be obtained in a quicker way if hydrochloride acid was used instead of potassium hydroxide, but no experimental details were reported.

Therefore, we decided to improve the reduction of 1-nitrocarbazole since the nitro group is so easily reduced to the amino group (see Scheme II, reaction (a)). Thus, a standard set of experimental conditions was adopted. The reduction of 1-nitrocarbazole was performed separately in two different solvents: methanol in the presence of catalytic amount of HCl and acetic acid. In both cases, zinc dust was added in excess and the solutions were heated at 60°. The yield of the product was determined by gc after an appropriate time. When the reaction was performed in acidic methanol solution the reduction process occurs in 10 minutes while in acetic acid solution the reduction requires a longer period of time, *ca*. 30 minutes. It is noteworthy that the chemical yield of the amino compound was improved and, in both solvents, a 95% yield was obtained. In this synthesis we confirmed that the reductive reaction of 1-nitrocarbazole could be achieve in mild conditions in methanol solution in the presence of zinc dust and catalytic amounts of hydrochloride acid.

The bromination reaction of 2-hydroxycarbazole was carried out with *N*-bromosuccinimide in a molar ratio (1:1.1) at room temperature according to the general procedure described in Experimental. We obtained in a simple and clean synthesis 3-bromo-2-hydroxycarbazole (**4c**) in 42.1 % (see Scheme II, reaction (b)).

Faulkner *et al*. [30] have introduced the *N*-bromosuccinimide – silica gel reagent as a convenient reagent system for the bromination of carbazole and related compounds. Also, we have introduced the N-chlorobenzotriazole – silica gel reagent as a useful chlorination method for carbazole and C-substituted carbazoles [24]. Nevertheless, when we performed the bromination reaction of 2-hydroxycarbazole according to the general procedure in the presence of silica – gel (1 g), the reaction became slower and no improvement on the chemical yield was observed. When the bromination reaction of 2-hydroxycarbazole was conducted in our experimental conditions, but at –18°, 3-bromo-2-hydroxycarbazole was obtained in 45% yield as the main product together with a significant amount of 1-bromo-2-hydroxycarbazole (>10%). Therefore,

Scheme II



diminishing the reaction temperature did not improve the chemical yield and product selectivity was not observed.

The introduction of methyl groups into a primary or secondary amine by reductive alkylation with formaldehyde and formic acid derivatives, the Clarke-Eschweiler method [31], has proved to be a useful method for the preparation of tertiary methylated amines. In some cases, however, complex mixtures have resulted from the multiplicity of side reactions that can take place [32]. Borch *et al*. [33] have introduced a novel method for the methylation of "reactive" and "unreactive" amines with aqueous formaldehyde and sodium cyanoborohydride. In order to obtain the tertiary methylated 3-amino-N-ethylcarbazole, in a mild and efficient process, we selected the last method to carry out the reductive methylation reaction.

Reaction of 3-amino-*N*-ethylcarbazole (**3g**) with aqueous formaldehyde and $NaBH_3CN$ in acetonitrile at room temperature according to the general procedure described in Experimental afforded, with high purity, 98% yield of the methylated amine **3j** (see Scheme II, reaction (c)). When the same reaction was performed in methanol as solvent a mixture of starting material and partially methylated amine were obtained. Therefore, acetonitrile proved to be the solvent of choice.

The direct formation of the aryl-alkyl or heteroaryl-alkyl carbon-carbon bond has found relatively few applications. This generally involves the reaction between an alkyl halide and a metallated (hetero) arene, in most cases under catalysed conditions [34]. The attack of an aryl (or heteroaryl) cation onto the electron rich alkene is an attractive alternative, in view of the facile reaction of electrophiles with such derivatives. This contrasts with the fact that there are practically no methods for the generation of aryl (or heteroaryl) cations except those of purely spectroscopic interest.

Albini *et al*. [35] have recently found that irradiation of chloro and fluoroanilines causes efficient heterolysis of the carbon-halogen bond and the resulting amino phenylium cation can be trapped in the presence of alkenes, benzene and five-membered heterocyclic compound. Therefore, we thought it worthwhile to extend the reaction to polycyclic heteroaromatic compounds such as 3-bromocarbazole (Scheme II, reaction (d)).

Photolysis of 3-bromocarbazole and isoprenyl acetate with $\lambda > 300$ nm in acetonitrile caused cleavage of the C-Br bond and gave carbazole along with 3-(2-oxopropyl) carbazole (**3i**) (see Scheme II, reaction (d)). Acidity was increased during the photoreaction and this caused the formation of coloured products and of a polymeric film on the reactor vessel, resulting in the interruption of the reaction because of the light-filter effect. However, stirring solid potassium carbonate in the reaction vessel during the irradiation allows for control the evolved acidity. Under these conditions coloration was minimized, the reaction proceeded with up to 85% conversion and compound (**3i**) was formed and isolated in good yield (60%). This smooth reaction gives selectively the 3-alkylsubstituted carbazole in a reasonable yield and appears to be a viable entry to such derivatives.

Correlations of ^1H nmr Chemical Shifts.

Assignments of the ^1H and ^{13}C chemical shifts were based on consideration of peak intensity, peak multiplicity under off-resonance ^1H decoupling and with complete ^1H coupling. All assignments were verified by 2D-NMR spectroscopy. ^1H-^{13}C heteronuclear multiple-quantum correlations (XHCORRDC) were measured at 300 K on a Bruker AM-500 spetrometer. Spectra were acquired using 2048 Hz per point in the F2 dimension (spectral width of 15151.52 Hz), and 128 Hz per point in the F1 dimension (spectral with 2551.02 Hz).

Tables I-IV list the proton chemical shifts, accurate to 0.02 ppm.

The ^1H chemical shifts for Series 1–4 were assigned in a straightforward manner with very few ambiguities. A wide singlet is usually present for NH of compounds in Series 2, 3 and 4, while for compounds of Series 4 another wide singlet was observed and was assigned to the OH group.

The ^1H signals appearing downfield in the range of 7.90 – 8.50 ppm were assigned to 4-H and 5-H in view of the

Table I

^1H Chemical Shifts of *N*-Substituted Carbazoles (Series 1) [a]

Compound	R	1-H 8-H	2-H 7-H	3-H 6-H	4-H 5-H	Others
1a	H	7.16	7.48	7.36	8.10	
1b	CH_3	7.20	7.45	7.35	8.15	3.86 (CH_3)
1c	CH_2Ph	7.21	7.43	7.34	8.18	7.41 (12-H and 14-H); 7.37 (11-H and 15-H); 7.23 (13-H); 5.55 (CH_2)
1d	Ph	7.27	7.44	7.34	8.13	7.40 (12-H and14-H); 7.38 (11-H and 15-H); 7.26 (13-H)
1e	$COCH_3$	8.22	7.46	7.40	8.00	2.88 (CH_3)
1f	COPh	7.62	7.46	7.34	8.00	7.70 (11-H and 15-H); 7.54 (12-H and 14-H); 7.28 (13-H)

[a] Values in parts per million (ppm). Internal reference: Tetramethylsilane.

Table II

^{1}H Chemical Shifts of 1-Substituted Carbazoles (Series 2) [a]

Compound	X	2-H	3-H	4-H	5-H	6-H	7-H	8-H	Others
2b	Cl	7.42	7.20	7.95	8.04	7.58	7.42	7.15	
2c	Br	7.50	7.40	7.99	8.06	7.52	7.42	7.16	
2d	I	7.67	6.98	8.13	8.09	7.61	7.43	7.20	
2e	COPh	8.12	7.52	8.36	8.11	7.36	7.48	7.19	7.83 (11-H and 15-H); 7.52 (12-H and 14-H); 7.30 (13-H)
2f	NO_2	8.24	7.35	8.62	8.31	7.38	7.46	7.13	
2g	NH_2	6.75	7.02	7.55	7.99	7.39	7.33	7.15	

[a] Values in parts per million (ppm). Internal reference: Tetramethylsilane.

Table III

^{1}H Chemical Shifts of 3-Substituted Carbazoles (Series 3) [a]

Compound	X	1-H	2-H	4-H	5-H	6-H	7-H	8-H	Others
3b	Cl	7.05	7.36	7.95	7.85	7.60	7.42	7.15	
3c	Br	7.40	7.50	8.35	8.09	7.61	7.43	7.16	
3d	I	7.37	7.65	8.51	8.15	7.52	7.43	7.18	
3e	COPh	7.54	8.10	8.59	7.92	7.50	7.43	7.19	7.54 (12-H and 14-H); 7.86 (11-H and 15-H); 7.30 (13-H)
3f	NO_2	7.58	8.29	9.15	8.36	7.51	7.45	7.13	
3g	NH_2	7.28	6.83	7.36	7.94	7.42	7.37	7.18	
3h	$NHCOCH_3$	7.31	7.48	8.24	8.03	7.43	7.36	7.18	2.87 (CH_3)
3i	CH_2COCH_3	7.23	7.30	7.92	8.06	7.42	7.37	7.16	3.90 (CH_2); 2.20 (CH_3)
3j	NMe_2	7.32	7.13	7.55	8.08	7.44	7.19	7.36	3.02 (NCH_3); 4.32 (CH_2); 1.41 (CH_3)

[a] Values in parts per million (ppm). Internal reference: Tetramethylsilane.

Table IV

^{1}H Chemical shifts of 3-Substituted-2-hydroxycarbazoles (Series 4) [a]

Compound	X	1-H	3-H	4-H	5-H	6-H	7-H	8-H	Others
4a	H	6.80	6.64	7.88	7.92	7.35	7.22	7.10	
4b	Cl	7.05	-	8.06	7.97	7.38	7.27	7.08	
4c	Br	7.07	-	8.15	7.93	7.38	7.28	7.09	
4d	$COCH_3$	6.86	-	8.41	7.97	7.38	7.27	7.13	2.79 (CH_3)
4e	COPh	6.98	-	8.24	7.97	7.37	7.28	7.13	7.75 (11-H and 15-H); 7.64 (12-H and 14-H); 7.32 (13-H)
4f	SO_2CH_3	6.85	-	8.42	7.95	7.38	7.27	7.15	3.38 (CH_3)
4g	SO_2Ph	6.87	-	8.44	7.93	7.39	7.27	7.14	7.70 (12-H and 14-H); 7.90 (11-H and 15-H); 7.25 (13-H)
4h	NO_2	7.24	-	9.11	8.40	7.45	7.70	7.70	

[a] Values in parts per million (ppm). Internal reference: Tetramethylsilane.

known deshielding at *peri*-positions for compounds in Series 1–4.

In general, introduction of a substituent on one benzene ring of the carbazole moiety produces no effect on the chemical shifts of the hydrogen of the other benzene ring (Series 2, 3 and 4). For *N*-substituted carbazoles, the substitutent effect applies on both benzene rings owing to the molecular symmetry of the carbazole moiety.

The aromatic protons of all the compounds in Series 2, 3 and 4 afford first order spectra, except for *N*-substituted carbazoles (Series 1). It is noteworthy to mention that for *N*-phenyl, *N*-benzoyl and *N*-acetylcarbazole (Series 1), 1-H and 8-H appear downfield as a result of the proximity of these protons to the *N*-substituent leading to van der Waals deshielding and/or anisotropic effects.

The correlation of 4-H and 2-H of carbazole derivatives in Series 2 with the resonance parameter (σ°_R) afforded positive ρ_R values: 1.53 (r^2: 0.949) and 1.93 (r^2: 0.998), respectively, but no such correlations was obtained when the inductive parameters (σ_1) were used. These results show that the substituent effect is transmitted from the variable substituent, X, to a larger extent to 2-H than to 4-H. Also, we correlated the 4-H chemical shifts of carbazoles in Series 2 with the hydrogen chemical shifts in the *para* position relative to the variable substituent of the monosubstituted benzene (Lynch correlations). The data

clearly reveal that the transmission of the substituent effect is enhanced more in the carbazole moiety than in the monosubstituted benzene, which is evident from the value of the slope obtained, 1.39 (r^2: 0.998).

Similar analysis was carried out with carbazoles of Series 3 and 4. Thus, in Series 3, the 4-H and 2-H afforded reasonable linear correlations with the σ°_R parameter. The slopes values are ρ_R (4-H): 2.84 (r^2: 0.969) and σ_R (2-H): 2.08 (r^2: 0.982). It is noteworthy that the ρ_R values obtained from the correlations of σ°_R with 2-H in Series 2 and in Series 3 are within experimental error. This result shows clearly that the transmission of the substituent effect operates to a similar extent in both Series.

The 4-H chemical shifts of carbazoles in Series 4 were correlated to σ°_R constant and afforded an ρ_R value of 0.91 (r^2: 0.984). Lynch correlation was also carried out between the 4-H chemical shifts of Series 4 and the 4-H chemical shifts of Series 3. A good linear correlation was obtained and the slope value was 0.83 (r^2: 0.980). This value clearly shows that the chemical shift of 4-H in Series 3 is influenced to a larger extent than 4-H of Series 4 by the variable substituent.

Finally, it is noteworthy to mention that the chemical shift of 3-H (Series 2), 1-H (Series 3) and 1-H (Series 4) do not afford reasonable correlations with both parameters, σ_I and σ°_R, due to a noticeable spread on the data.

Correlations of ^{13}C nmr Chemical Shifts.

The ^{13}C nmr chemical shifts of carbazoles in Series 1, 2, 3 and 4, accurate to 0.05 ppm, are listed in Tables V – VIII.

The ^{13}C chemicals shift of 9a-C, 1-C and 3-C of carbazoles in Series 1 afforded satisfactory correlations with σ_I and σ°_R constants (see Table IX). The sign of the σ values show normal substituent effects on 1-C and 3-C and inverse substituent effects on 9a-C. The inverse substituent effect could be ascribed to the involvement of a localized π-polarization mechanism in this system, resulting in separate polarization of the substituent and the carbazole moiety in Series 1 [36].

Also, this separate π-polarization could be additionally increased taking into account that the substituents such as

Table V

^{13}C Substituent Chemical Shifts of *N*-Substituted Carbazoles (Series 1) [a]

Compound	R	1-C 8-C	2-C 7-C	3-C 6-C	4-C 5-C	4a-C 4b-C	9a-C 8a-C	Others
1a	H	110.8	125.3	118.4	119.4	122.4	139.4	
1b	Me	108.1	125.2	118.3	119.7	122.1	140.4	13.6 (CH_3)
1c	CH_2Ph	109.1	126.6	119.4	120.5	123.2	140.9	46.7 (CH_2); 137.4 (10-C); 126.0 (11-C and 15-C); 127.6 (12-C and 14-C); 128.4 (13-C)
1d	Ph	110.0	126.1	120.1	120.5	123.6	139.7	141.2 (10-C); 127.3 (11-C and 15-C); 130.0 (12-C and 14-C); 127.6 (13-C)
1e	$COCH_3$	116.4	127.4	123.7	120.2	125.8	138.3	170.0 (CO); 27.4 (CH_3)
1f	COPh	115.6	127.2	123.3	119.6	125.9	139.2	169.4 (CO); 135.7 (10-C); 128.7 (11-C and 15-C); 128.8 (12-C and 14-C); 132.1 (13-C)
1g	CHO	116.5	127.2	124.2	120.1	125.7	137.1	173.6 (CO)
1h	$COCF_3$	116.1	125.4	127.7	119.8	126.8	137.4	171.2 (CO); 115.1 (CF_3)

[a] Values in parts per million (ppm). Internal reference: Tetramethylsilane.

Table VI

^{13}C Substituent Chemical Shifts of 1-Substituted Carbazoles (Series 2) [a]

Compound	R	1-C 8-C	2-C 7-C	3-C 6-C	4-C 5-C	4a-C 4b-C	9a-C 8a-C	Others
2b	Cl	116.5	126.6	120.2	118.7	125.0	140.3	
		111.0	125.1	120.0	120.8	122.4	139.3	
2c	Br	110.5	127.8	122.8	119.6	123.6	140.6	
		111.1	126.2	118.9	120.6	122.4	139.3	
2d	I	72.5	134.0	120.0	120.4	123.0	141.4	
		111.7	126.1	119.2	120.6	122.6	139.5	
2e	COPh	120.1	125.6	119.3	126.5	124.8	138.2	130.6 (10-C); 128.1 (11-C and 15-C); 197.4 (CO);
		110.3	125.8	118.3	117.8	122.1	143.0	131.3 (13-C); 129.2 (12-C and 14-C).
2f	NO_2	140.6	121.6	127.9	132.8	130.9	131.6	
		112.6	127.1	118.2	120.5	121.4	127.1	
2g	NH_2	134.6	115.6	122.8	114.8	127.7	143.7	
		115.9	123.7	124.3	129.3	128.0	143.7	

[a] Values in parts per million (ppm). Internal reference: tetramethylsilane.

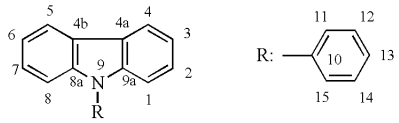


Figure 1. Atom numbering of carbazole and its derivatives.

phenyl, formyl, acetyl, benzoyl and trifluoroacetyl groups are twisted from the plane of the carbazole moiety as confirmed by calculations using the PM3 semi empirical method. Thus, the twisted conformation diminishes the resonance interaction between the carbazole moiety and the substituents while a significant π-polarization interaction is displayed.

It is pertinent to note that, in general, the amide group (-NHCOR) have large resonance interaction when the nitrogen and the acyl group are coplanar and, simultaneously the π-polarization interaction is overshadowed [37].

As can be seen in Table IX, the r_I and r_R values are roughly similar in terms of the absolute value and the sign for 9a-C, 1-C and 3-C, respectively, for carbazoles in Series 1. This suggest, that the inductive and resonance substituent effects transmit well even if the substituents are twisted from the plane of the carbazole moiety. Similar results and trends were also reported for 4-substituted phenylthiol acetates, benzoates and cinnamates [36].

In addition, we have analysed the substituent effects on 4-C of carbazoles in Series 2 and on 9a-C of carbazoles in

Table VII

^{13}C Substituent Chemical Shifts of 3-Substituted Carbazoles (Series 3) [a]

Compound	R	1-C 8-C	2-C 7-C	3-C 6-C	4-C 5-C	4a-C 4b-C	9a-C 8a-C	Others
3b	Cl	113.0	126.2	123.4	120.4	122.8	139.4	
		110.7	125.6	117.9	119.8	122.9	138.2	
3c	Br	112.8	127.8	110.5	122.6	121.4	140.1	
		111.1	126.2	118.9	120.6	124.4	138.4	
3d	I	113.3	133.3	81.2	128.6	125.1	139.7	
		111.0	126.2	118.9	120.5	121.1	138.7	
3e	COPh	111.8	129.6	128.5	120.9	123.3	141.2	128.6 (10-C); 130.3 (11-C and 15-C); 198.4 (CO)
		111.0	124.6	118.2	120.3	123.7	139.4	132.4 (13-C); 128.7 (12-C and 14-C).
3f	NO_2	111.7	121.1	143.1	116.9	122.2	140.8	
		110.9	127.3	120.0	120.9	121.9	139.6	
3g	NH_2	109.2	115.1	132.8	104.2	121.9	141.4	
		108.6	117.5	119.9	125.0	122.8	139.7	
3h	$NHCOCH_3$	112.4	123.6	133.7	116.9	126.8	141.2	17.6 (CH_3); 173.6 (CO).
		112.3	122.6	124.4	129.7	127.0	144.4	
3i	CH_2COCH_3	110.9	127.1	125.3	121.0	123.8	139.7	29.1 (CH_3); 51.3 (CH_2); 207.6 (CO).
		110.7	126.1	119.5	120.4	123.1	138.7	
3j	NMe_2	108.9	115.4	134.2	105.4	122.9	145.4	
		108.4	118.0	122.9	125.4	123.5	140.5	

[a] Values in parts per million (ppm). Internal reference: tetramethylsilane.

Table VIII

^{13}C Substituent Chemical Shifts of 3-Substituted-2-hydroxycarbazoles (Series 4) [a]

Compound	R	1-C 8-C	2-C 7-C	3-C 6-C	4-C 5-C	4a-C 4b-C	9a-C 8a-C	Others
4a	H	96.4	156.4	108.3	120.7	115.2	141.4	
		110.3	123.6	118.3	118.8	123.0	139.6	
4b	Cl	97.4	157.5	114.9	121.8	116.8	143.6	
		110.7	123.9	118.1	119.2	123.1	139.8	
4c	Br	97.3	152.2	101.3	123.8	116.7	140.3	
		110.5	124.4	118.6	119.4	122.0	139.8	
4d	$COCH_3$	97.3	162.3	119.4	120.7	116.8	145.4	31.9 (CH_3); 203.7 (CO)
		110.7	125.9	119.6	120.6	123.6	140.3	
4e	COPh	97.6	172.5	116.5	125.9	116.9	145.2	138.1 (10-C); 127.6 (11-C and 15-C); 198.9 (CO)
		110.8	128.4	119.8	120.7	122.7	140.6	132.4 (13-C); 129.5 (12-C and 14-C)
4f	SO_2Ph	98.1	154.2	116.0	122.8	117.5	145.6	142.6 (10-C); 126.7 (11-C and 15-C)
		110.8	125.9	119.8	120.2	122.0	140.2	132.9 (13-C); 129.4 (12-C and 14-C)
4g	NO_2	97.2	151.1	128.3	120.1	119.8	147.4	
		110.6	124.0	118.7	118.8	122.2	140.5	

[a] Values in parts per million (ppm). Internal reference: tetramethylsilane.

Series 3 and 4, using the resonance parameter (σ°_{R}). Satisfactorily linear correlations were obtained and the results are shown in Table X. The magnitude of the σ_R value clearly reveals that the resonance effects are transmitted from the variable substituent X, to carbons in the *para* position (4-C and 9a-C, respectively) to a larger extent in Series 2 and 4 than in Series 3. The enhanced transmission in Series 2 and 4 should probably be ascribed to a favourable intramolecular hydrogen bonding between the variable substituents, such as COMe, COPh, SO_2Ph, NO_2 and adjacent NH and/or OH groups. This interaction, which is, of course, not possible in Series 3, could lead to an enhanced coplanarity of the substituents and hence, to an effective p-resonance transmission from the substituent to the carbazole moiety.

We also calculated the optimised geometries of carbazoles in Series 2, 3 and 4 using the PM3 semi empirical method. The calculations show the feasibility of the intramolecular hydrogen bonding between the variable substituents (COPh, COMe, SO_2Ph and NO_2) and the NH and OH groups of carbazoles in Series 2 and 4, respectively. Also, the semi empirical calculations show the non-coplanarity of the variable substituents with the carbazole moiety in Series 3. The coplanarity effect together with the intramolecular hydrogen bonding was observed in other aromatic systems [38,39].

The substituent effects on the *ipso*-carbon of carbazole derivatives of Series 2, 3 and 4 were also analysed according to Lynch correlation and the data are listed in Table XI to facilitate comparison. The data clearly show that the chemical shifts of 1-C (Series 2) and 3-C (Series 3) are influenced to a larger extent than the *ipso*-C of monosubstituted benzenes by the variable substituent (see the slope values in Table XI). The correlation results of 3-C chemical shift of Series 4 listed in Table XI reveal almost identical trends in the transmission of substituent effects as it is observed for monosubstituted benzenes, which is evident from the value of the slope, 1.07 (r^2: 0.996).

Charge Density and Chemical shifts.

We calculated the net atomic charge density of carbazoles in Series 1, 2, 3 and 4 by using the semi empirical PM3 method. Taking into account that there is a linear relationship between the measured ^{13}C chemical shift and the net atomic charge density, we attempted to correlate the ^{13}C substituent chemical shifts of carbons at *para* and *ipso* position and the net atomic charge on the same carbon atoms in carbazoles of Series 1, 2, 3 and 4. The net atomic charge density values of 9a-C, 1-C and 3-C (Series 1); 1-C and 4-C (Series 2); 3-C and 9a-C (Series 3) and 3-C and 9a-C (Series 4), computed by PM3 calculations, are shown in Table XII.

Figure 2 shows the linear dependence between the ^{13}C chemical shifts of 9a-C, 1-C and 3-C and the net atomic charge density on the same carbon atoms of *N*-substituted

Table IX

Results of Hammett Correlations of 9a-C, 1-C and 3-C Chemical shifts of *N*-Substituted Carbazoles (Series 1) using σ_I and σ°_{R} Constants

Atom	ρ_I	r^2	ρ_R	r^2
9a-C	- 7.6	- 0.986	-8.1	- 0.933
1-C	22.8	0.944	26.0	0.978
3-C	20.2	0.989	22.2	0.989

Table X

Results of Hammett Correlations of 9a-C and 4-C Chemical shifts of Carbazoles in Series 2, 3 and 4 using σ°_{R} Constants

Series	Atom	ρ_R	r^2
2	4-C	28.8	0.923
3	9a-C	7.2	0.972
4	9a-C	15.7	0.977

Table XI

Substituent Effect on the Chemical Shift Values of *ipso*-Carbon (C_i) of Carbazoles in Series 2, 3 and 4 and C_i of Monosubstituted Benzene

R	Series 2 1-C	Series 3 3-C	Series 4 3-C	Monosubstituted benzene (C_i)
NH_2	-	12.7	-	19.2
NHCOMe	-	13.6	-	11.1
H	0	0	0	0
Cl	5.7	5.0	6.6	6.4
Br	-8.2	-7.9	-7.0	-5.4
I	-38.3	-37.2	-	-32.2
COMe	-	-	10.8	9.3
COPh	9.3	10.1	8.2	9.3
SO_2Ph	-	-	7.7	15.6
NO_2	29.8	24.7	20.0	19.6
Slope	1.3	1.3	1.1	-
r^2	0.982	0.984	0.996	-

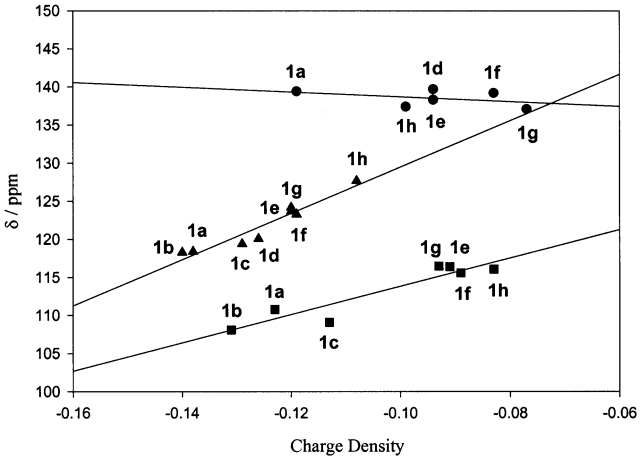


Figure 2. Correlations between ^{13}C chemical shift and net atomic charge density of *N*-substituted carbazoles (Series 1). Symbols: ● 9a-C; ■ 1-C and ▲ 3-C. Numbers are those of the compounds listed in Scheme I.

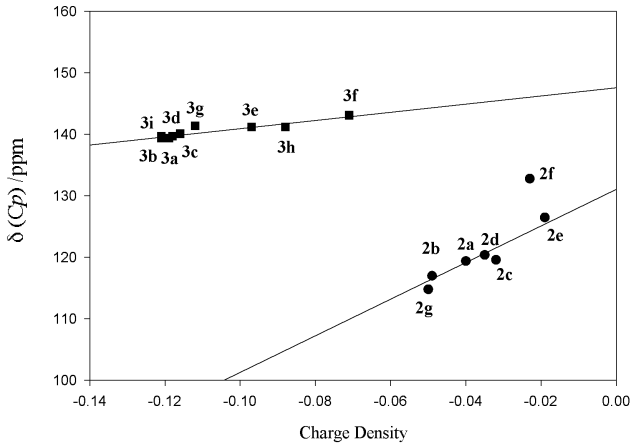


Figure 3. Correlations between ^{13}C chemical shift at the *para*-position (C*p*) and the net atomic charge density at the same carbon atom of carbazoles in: ● Series 2 (4-C) and ■ Series 3 (9a-C). Numbers are those of the compounds listed in Scheme I.

to those obtained in the Hammett correlations for *N*-substituted carbazoles (compare Table XIII with Table IX). These results show that the charge density predicts nicely the substituent effect on the ^{13}C chemical shifts of *N*-substituted carbazoles in Series 1. Also, this relationship can be employed for the estimation of electron densities on 9a-C, 1-C and 3-C in Series 1 using ^{13}C nmr data or *vice versa*.

In addition, we have correlated the ^{13}C chemical shifts of carbons at *para* position of carbazoles in Series 2, 3 and 4 with the net charge density at the same carbon atoms and Figure 3 shows the linear dependence obtained for 4-C (Series 2) and 9a-C (Series 3). This analysis afforded satisfactory linear correlations and the slope, intercept and r^2 values are shown in Table XIII. Also, this analysis shows that the net atomic charge density gives good prediction of the substituent effect on the ^{13}C chemical shifts of C-substituted carbazoles in Series 2, 3 and 4 (compare the sign of the slope values shown in Table XIII with those listed in Table X).

Table XII

Net Atomic Charge Density Values at 1-C, 3-C and 9a-C in Series 1, 1-C and 4-C in Series 2 and 3-C and 9a-C in Series 3 and 4 by PM3 Calculations

	Series 1			Series 2		Series 3		Series 4	
R	1-C	3-C	9a-C	1-C	4-C	3-C	9a-C	3-C	9a-C
NH_2	-	-	-	-0.082	-0.081	-0.101	-0.112	-	-
NMe_2	-	-	-	-	-	-0.058	-0.148	-	-
$NHCOCH_3$	-	-	-	-	-	-0.110	-0.088	-	-
Cl	-	-	-	-0.133	-0.049	-0.146	-0.121	-0.194	-0.077
Br	-	-	-	-0.131	-0.032	-0.141	-0.116	-0.198	-0.072
I	-	-	-	-0.150	-0.035	-0.159	-0.118	-	-
$COCH_3$	-0.091	-0.120	-0.094	-	-	-	-	-0.310	-0.042
COPh	-0.089	-0.119	-0.083	-0.179	-0.019	-0.190	-0.097	-0.213	-0.064
SO_2Ph	-	-	-	-	-	-	-	-0.614	-0.032
NO_2	-	-	-	-0.446	-0.023	-0.458	-0.071	-0.452	-0.039
CHO	-0.093	-0.120	-0.077	-	-	-	-	-	-
$COCF_3$	-0.083	-0.108	-0.099	-	-	-	-	-	-
CH_3	-0.131	-0.140	-0.109	-	-	-	-	-	-
Ph	-0.177	-0.126	-0.094	-	-	-	-	-	-
CH_2Ph	-0.113	-0.129	-0.088	-	-	-	-	-	-
CH_2COCH_3	-	-	-	-	-	-0.095	-0.116	-	-
H	-0.123	-0.138	-0.119	-0.123	-0.040	-0.138	-0.119	-0.177	-0.076

Table XIII

Results of the Correlations of the ^{13}C Chemical Shift and Net Atomic Charge Density of Carbazoles in Series 1, 2, 3 and 4

Series	Correlation	Slope	Intercept	r^2
1	9a-C	-71.5	135.6	0.984
	1-C	200.8	132.4	0.948
	3-C	306.4	159.9	0.954
2	4-C	241.7	129.8	0.997
	1-C	1168.4	261.9	0.951
3	9a-C	53.7	145.9	0.962
	3-C	825.2	222.3	0.900
4	9a-C	56.8	148.3	0.949

carbazoles (Series 1). The results obtained from these correlations are listed in Table XIII. It is noteworthy that the sign of the slope values obtained in these correlations are similar

Finally, we have also attempted the correlation of the ^{13}C chemical shifts at the *ipso*-position of carbazoles in Series 2, 3 and 4 with the net atomic charge density at the same carbon atoms. Figures 3 shows satisfactorily linear correlations when the nitro group is excluded from the correlation analysis due to its deviation from linearity. This deviation suggests a redistribution of the electron density on the carbazole moiety due to the influence of the nitro group, a strong withdrawing substituent. Thus, the presence of a nitro group attached to the carbazole moiety can lead to an increased contribution of the dipolar resonance structures as it is illustrated for 3-nitrocarbazole in Figure 4.

Analysis of the ^1H-nmr chemical shifts of carbazoles in Series 1, 2, 3 and 4 shows that the substituent effect is well transmitted and gives good linear correlations with the σ°_R substituent Hammett constants. The substituent chemical

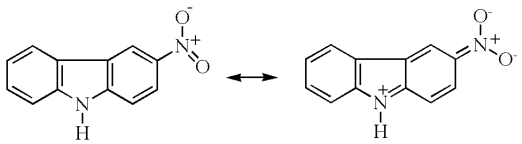


Figure 4. Dipolar resonance structure of 3-nitrocarbazole.

shift of 9a-C of carbazoles in Series 1 show "inverse" behaviour due to a localized π-polarization mechanism, whereas a "normal" behaviour is observed for the substituent chemical shift of 3-C of carbazoles in the same Series. The Hammett substituent analysis on carbons in *ipso* and *para* position of carbazoles in Series 2, 3 and 4 gives satisfactory linear correlations using the resonance parameters (σ°_R).

The ^{13}C chemical shifts of carbons at *ipso* and *para* position and the net atomic charge density computed by PM3 calculations at the same atoms for carbazoles in Series 1, 2, 3 and 4 give good linear correlations. Hence, the charge density predicts nicely the substituent effect on the ^{13}C-nmr chemical shifts of the compounds studied. Also, this relationship can be employed for the estimation of the ^{13}C chemical shifts using the net atomic charge density data or *vice versa*.

EXPERIMENTAL

Carbazole (**1a**), 2-hydroxycarbazole (**4a**), *N*-methylcarbazole (**1b**) and *N*-phenylcarbazole (**1d**) were purchased from Aldrich and were recrystallized from ethanol. 3-Amino-*N*-ethylcarbazole (**3g**) was purchased from Aldrich and was purified by silica gel column chromatography. 3-Acetamido-*N*-ethylcarbazole (**3h**) was prepared by acetylation of 3-amino-*N*-ethylcarbazole [40]. *N*-Acetylcarbazole (**1e**) [41], *N*-benzoylcarbazole (**1f**) [23], *N*-benzylcarbazole (**1c**) [42], 1-bromocarbazole (**2c**) and 3-bromocarbazole (**3c**) [30], 1-nitrocarbazole (**2f**) and 3-nitrocarbazole (**3f**) [26], 1-benzoylcarbazole (**2e**) and 3-benzoylcarbazole (**3e**) [23], 1-chlorocarbazole (**2b**), 3-chlorocarbazole (**3b**) and 3-chloro-2-hydroxycarbazole (**4b**) [24] and 1-iodocarbazole (**2d**) and 3-iodocarbazole (**3d**) [25] were prepared according to the procedures described in the literature. 3-Acetyl (**4d**), 3-benzoyl (**4e**) and 3-benzenesulphonyl-2-hydroxycarbazole (**4f**) were prepared by the photo-Fries rearrangement [28].

The ^1H nmr spectra were obtained at 200 MHz (Brucker spectrometer) for approximately 0.03 *M* solutions with TMS as internal reference. Broadband and off-resonance decoupled ^{13}C spectra were obtained at 200 MHz with the same apparatus for *ca* 0.5 *M* solutions with TMS as internal reference. The spectra of all the compounds were measured in $CDCl_3$ except for compounds **2f** (Series 2), **3c** and **3f** (Series 3) and **4g** (Series 4) where DMSO-d_6 was employed to overcome solubility difficulties. A pulse angle of 37.5° (5 μs) and a repetition time of 3.7 s were used at room temperature (20 – 21°C). 2D nmr C/H shift correlated spectra were obtained using the standard Bruker program (HETCOR; Programe name: XHCORRDC.AUR) at 500 MHz, with a spectral width of 2551.02 Hz in the ^1H direction (resolution 128 Hz per point) and 15151.52 Hz in the ^{13}C direction (resolution 2048 Hz per point).

Substituent parameter correlations were obtained using the program Sigma Plot 4.01. In all cases the confidence level was 99%. Sources of the substituent constants are as follow: σ_I [43-45]; σ°_R [2, 43, 45 and 46].

Synthesis of New Carbazole Derivatives.

1-Aminocarbazole (**2g**).

To a stirred solution of 1-nitrocarbazole (**2f**) (100 mg, 0.47 mmol) in acetic acid (10 ml), 400 mg of zinc dust was added in one portion. Then, hydrochloride acid 37 % (0.04 ml) was added to the stirred solution. The yellowish solution was heated at 60° until it became colourless (approximately 10 – 15 minutes) and was left to cool at room temperature. The colourless solution was poured dropwise into an alkaline aqueous solution (pH = 13). The alkaline solution was extracted with chloroform (3x10 ml), the organic layers were combined and washed with water (2x10ml), dried with Na_2SO_4, filtered and evaporated *in vacuo* to give a brownish residue. The residue was separated by column chromatography (silica gel, hexane – ethyl acetate (7:3)) to give 1-aminocarbazole (**2g**) in 95% yield. This compound was obtained as white needles, mp 226 – 227° (lit. 226 – 228° [29]); ^1H nmr (deuteriochloroform): δ 7.99 (d, 1 H, 5–H, J = 7.8 Hz), 7,55 (dd, 1 H, 4–H, J = 0.7, 7.8 Hz), 7.39 (d, 1 H, 8–H, J = 8.2 Hz), 7.33 (dt, 1 H, 6–H, J = 6,8, 7.8 Hz), 7.15 (t, 1 H, 7–H, J = 6.8, 8.2 Hz), 7.02 (t, 1 H, 3–H, J = 7,8 Hz), 6.75 ppm (dd, 1 H, 2–H, J = 0.7, 7.7 Hz); ^{13}C nmr (deuteriochloroform): δ 143.7 (9a–C), 143.2 (8a–C), 134.6 (1–C), 129.3 (5–C), 128.0 (4b–C), 127.7 (4a–C), 124.2 (6–C), 123.7 (7-C), 122.8 (3–C), 115.9 (8–C), 115.6 (2-C), 114.8 ppm (4–C).

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.12; H, 5,49; N, 15,38. Found: C, 79.22; H, 5.47; N, 15.36.

3-(*N,N*-dimethylamino)-*N*-ethylcarbazole (**3i**).

To a stirred solution of 3-amino-*N*-ethylcarbazole (1.05 g, 5 mmole) and 8 ml (25 mmole) of 37% aqueous formaldehyde in 15 ml of acetonitrile was added 500 mg (8 mmole) of sodium cyanoborohydride. A vigorous exothermic reaction ensued, and a dark residue separated. The reaction mixture was stirred for 30 minutes and glacial acetic acid was added dropwise until the solution tested neutral on wet pH paper. Stirring was continued for an additional 45 minutes, glacial acetic acid being added occasionally to maintain the pH near neutrality. The solvent was evaporated at reduced pressure, and 20 ml of 2 *N* KOH was added to the residue. The resulting mixture was extracted with ether (3x10ml). The combined ether extracts were dried over K_2CO_3 and evaporated *in vacuo* to give 1.17 g (98%) of 3-*N,N*-dimethylamino-*N*-ethylcarbazole as a white powder. On recrystallization from ethanol give 1.02 g (85%) of compound (**3j**) as colourless needles, mp 183 –184°; ^1H nmr (deuteriochloroform): δ 8.08 (d, 1 H, 5-H, J = 7.8 Hz), 7.55 (d, 1 H, 4-H, J = 2.4 Hz), 7.44 (t, 1 H, 6-H, J = 7.8 Hz), 7.36 (d, 1 H, 8-H, J = 8 Hz), 7.32 (d, 1 H, 1-H, J = 8.8 Hz), 719 (t, 1 H, 7-H, J = 8 Hz), 7.13 ppm (dd, 1 H, 2-H, J = 2.4, 8.8 Hz); ^{13}C nmr (deutriochloroform): δ 145.4 (9a-C), 140.5 (8a-C), 134.2 (3-C), 125.4 (5-C), 123.5 (4b-C), 122.9 (4a-C), 120.3 (6-C), 118.0 (7-C), 115.4 (2-C), 108.9 (1-C), 108.4 (8-C), 105.4 ppm (4-C).

Anal. Calcd. for $C_{16}H_{18}N_2$: C, 80.67; H, 7.56; N, 11.76. Found: C, 80.63; H, 7.58; N, 11.74.

3-Bromo-2-hydroxycarbazole (**4c**).

To a stirred solution of 2-hydroxycarbazole (0.55 mmole) in dichloromethane (10 ml) a solution of *N*-bromosuccinimide (0.60

mmole) in dichloromethane (5 ml) was added dropwise. The reaction was a stirred for an appropriate time in the absence of light at room temperature until tlc and gc indicated the reaction was completed. The reaction mixture was evaporated *in vacuo* and a yellowish solid residue was obtained. The residue was separated by column chromatography (silica–gel, hexane–ethyl acetate eluent mixtures) to give 3-bromo-2-hydroxycarbazole (**4c**) in 42% yield. This compound was obtained as white needles (ethanol), mp 195°; ^{1}H nmr (deuteriochloroform): δ 8.15 (s, 1 H, 4-H), 7.97 (s, 1 H, NH), 7.93 (d, 1 H, 5-H, J = 8.0 Hz), 7.38 (d, 1 H, 6-H, J = 8.0 Hz), 7.20 (m, 2 H, 7-H and 8-H), 7.07 (s, 1 H, 1 – H), 5.66 ppm (s, 1 H, OH); ^{13}C nmr (deuteriochloroform): δ 152.1 (2-C), 140.3 (9a-C), 139.8 (8a-C), 124.4 (7-C), 122.0 (4b-C), 119.3 (5-C), 118.6 (6-C), 116.7 (4a-C), 110.5 (8-C), 101.3 (3-C), 97.3 ppm (1-C).

Anal. Calcd. for $C_{12}H_8ONBr$: C, 54.96; H, 3.05; N, 5.34; Br 30.53; O, 6.11. Found: C, 55.01; H, 3.10; N, 5.26; Br, 30.21.

3-(2-Oxopropyl)carbazole (**3i**).

In a typical experiment, a solution of 100 mg (0.41 mmole) in 75 ml acetonitrile containing 0.83 ml (7.5 mmole, d: 0.909 mg/ml) was irradiated for 3 hours in an immersion well apparatus fitted with a high pressure mercury lamp (Hereaus, TQ-150-Z_3, 150 W, water cooled through a quartz jacket) after 15 minutes flushing with argon and maintaining a slow gas flux during the irradiation. Anhydrous potassium carbonate (250 mg) was added and the solution magnetically stirred during the experiment. The progress of the reaction was monitored by gc and tlc. The reaction mixture was filtered and the filtrate was evaporated *in vacuo* to obtain a brownish residue. The residue was separated by column chromatography (silica – gel, hexane ethyl acetate) to give compound (**3 i**) in 60% yield. This compound was obtained as white needles, mp 192°; ^{1}H nmr (deuteriochloroform): δ 8.06 (d, 1 H, 5-H, J = 8.0 Hz), 7.92 (d, 1 H, 4-H, J = 2.1 Hz), 7.46 (t, 1 H, 6-H, J = 8.0 Hz), 7.53 (d, 1 H, 8-H, J = 7.8 Hz), 7.30 (dd, 1 H, 2-H, J = 2.1, 8.4 Hz), 7.23 (d, 1 H, 1-H, J = 8.4 Hz), 7.16 (t, 1 H, 7-H, J = 7.8 Hz), 3.90 (s, 2 H, CH2), 2.2 ppm (s, 3 H, CH3); ^{13}C nmr (deuteriochloroform): δ 207.6 (CO), 139.7 (9a-C), 138.7 (8a-C), 127.1 (2-C), 126.1 (7-C), 125.3 (3-C), 123.8 (4a-C), 123.1 (4b-C), 121.0 (4-C), 120.4 (5-C), 119.5 (1-C), 110.7 (8-C), 51.3 (CH_2), 29.1 ppm (CH_3).

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.72; H, 5.83; N, 6.28; O, 7.17. Found: C, 80.75; H, 5.81; N, 6.29.

Calculations.

The ground state geometry, heat of formation and static charge distribution of carbazoles in Series 1 to 4 were calculated by using the semi empirical parameterised PM3 method as implemented in version of the HyperChem Program [47] which has proven to be effective in studies on molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

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