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NUCLEOPHILIC RECYCLIZATION OF β-CARBOLINES — NEW VARIANT OF THE SYNTHESIS OF THE CARBAZOLE RING

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UDC 547.759.3'836.3:542.938'953.2:543.422'51

The reaction of salts of 1,3-dimethyl-9H-pyrido[3,4-b]indole with hydroxide ions was examined within the framework of the Pariser—Parr—Pople (PPP) method. It is shown that the reaction may stop at the step involving the formation of an anhydro base (R = H) or lead to recyclization products (R = CH_3, C_2H_5), viz., carbazole derivatives. The calculated data are in good agreement with the experimental data.

The isomerizational recyclization of nitrogen-containing heteroaromatic systems (the Kost—Sagitullin reaction) has been well studied both experimentally [1, 2] and theoretically (for example, see [3]). Let us note that chief attention in the investigation of this reaction has been directed to the effects of chemical substitution in the pyridine fragment of the molecule [1, 2], including aza substitution [3, 4], on the effect of annelation [5] and the relationship between the aromatic character of the recyclized systems and the course of the process [3, 6], on the structure of the N-alkyl group [7] and the nucleophilic fragment in the molecule [1, 8], and on the dependence of the direction and rate of rearrangement on the experimental conditions and the nucleophilic agent used [9, 10]. Steric effects [11] and the structural aspects [12] of this recyclization have also been studied.

In the present research we studied the effect of a heterocyclic ring condensed with the pyridine ring on the rearrangement of 1,2,3-trialkylpyridinium salts. Except for a few examples in which the nitrogen atom of the pyridine fragment was common to both rings, as in the recyclization of indolizines to indoles [13], pyrimidoindoles to α-carbolines [14], and pyrazolopyrimidines to pyrazolopyridines [5], this problem has not been dealt with in the literature. As the subject of our investigation we selected the β-carboline system, in which a pyridine ring is condensed with an indole ring. In addition to the relative accessibility of this model, the selection of this system was dictated by the widely known biological activity of derivatives of isomeric carbolines. The β-carboline ring is included in the composition of many natural and synthetic alkaloids, such as brevicolline, which displays high ganglion-blocking activity, and yohimbine and reserpine, which have hypotensive activity [16, 17]. Derivatives of isomeric 1,2,3,4-tetrahydrocarbolines, which display cytostatic and psychotropic activity [18, 19], have anti-inflammatory, analgesic, and antipyretic effects [20]. The high biological activity of compounds of this class has stimulated research on the synthesis or isolation of these compounds from natural substances and their pharmacological screening in the last few decades. However, very little study has been devoted to the reactivities of carboline systems and their transformations under the influence of various reagents.

One of the possible pathways for the recyclization of the pyridine ring to a benzene ring is prior formation of anhydro bases by the action of hydroxide ions on the corresponding quaternary salts [1, 2]. This mechanism for rearrangement is confirmed indirectly by recyclization of an isolated anhydro base (1-methyl-2-acetonylidene-5-nitropyridine) [21]

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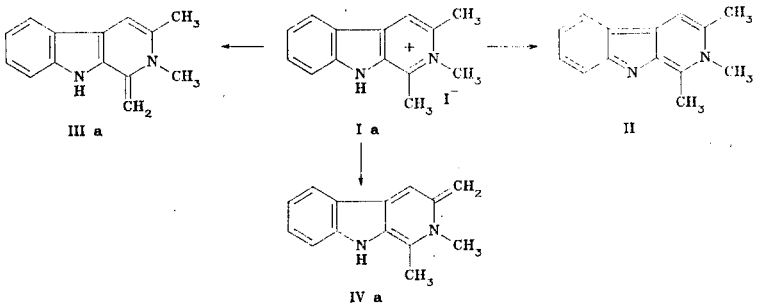
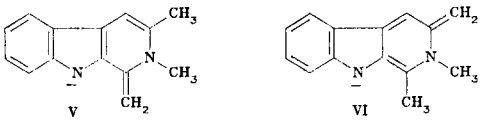
and by the results of x-ray diffraction analysis [12]. We therefore assume that the rearrangement of 1,3-dimethyl-9H-pyrido[3,4-b]indole methiodide (Ia) under the influence of alkali should also proceed through a step involving the formation of an anhydro base. Three variants of deprotonation to give the corresponding anhydro bases II-IV are possible in the action of hydroxide ions on Ia: splitting out of a proton from both the NH group of the indole fragment and from the two methyl groups bonded to the pyridine ring:



III a I a II IV a

The deprotonation processes are intimately associated with the labilities of the corresponding protons, and one can therefore solve the problem of the site of deprotonation by making comparative estimates of the CH and NH acidities of the methyl groups in the 1 and 3 positions and the NH group of the indole fragment of the Ia molecule. These estimates were made as described in [6]. For this, we performed quantum-chemical calculations by the Pariser–Parr–Pople (PPP) method (with the parametrization in [3, 6, 22]) of the anions obtained from IIIa and IVa by deprotonation of the nitrogen atom (V and VI):



V VI

The results of the calculations show that the charges on the nitrogen atoms of the indole fragments in anions V and VI are smaller than those on the corresponding methylene groups (–0.26237 and –0.30159 for V and –0.35489 and –0.42674 for VI, respectively). According to these data, the nitrogen atom of the indole fragment should be deprotonated first. In addition, this conclusion is confirmed by a comparison of the aromaticity indexes (the relative diamagnetic susceptibilities χ' [22]*) of II-IV. The calculations give the following values for these compounds: $\chi'_{II} = 2.73$, $\chi'_{III} = 1.81$, and $\chi'_{IV} = 1.38$. Consequently, of all of the anhydro bases, the most aromatic and therefore the most stable compound is II, the formation of which should be preferred. It should be noted that II is more aromatic than starting cation I and even 9H-pyrido[3,4-b]indole (VII)† itself (for comparison, $\chi'_I = 2.43$, and $\chi'_{VII} = 2.69$ [22]). In fact, we obtained anhydro base II in quantitative yield in the reaction of salt I with an alcohol solution of alkali. The IR spectrum of II does not contain absorption at 3400-3500 cm^{-1}, which constitutes evidence for deprotonation of the NH group of the indole part of the molecule. The fact that II is somewhat more aromatic than base VII evidently also explains the absence of dealkylation in the action of hydroxide ions on salt Ia, despite the fact that in cation I the positive π-electron charge on the nitrogen atom of the pyridine ring is higher than that on the indole nitrogen atom (Fig. 1). Anhydro base II does not undergo recyclization under the influence of hydroxide ions even under very severe conditions and is recovered unchanged from the reaction mixture.

If one examines the recyclization of anhydro base II within the framework of the traditional approach to the mechanism of this reaction [1], the next step in the action of hydroxide ions on anhydro base II should be the formation of anions V and VI. These anions, inasmuch as they are negatively charged particles, should not undergo attack by hydroxide ions, as evidenced by the residual π-electron charges on the carbon atoms of V and VI ($q_3 = -0.11440$ and $q_1 = -0.05187$, respectively). Consequently, these anions should not undergo opening of the pyridine ring and rearrangement under the influence of nucleophiles.

*Note that $\chi' = \chi^{\pi}/\chi^{\pi}_{C_6H_6}$ [23].

†It should be noted that the calculated ^{1}H NMR spectrum for VII, which reproduces the experimental data satisfactorily, is presented in [22].

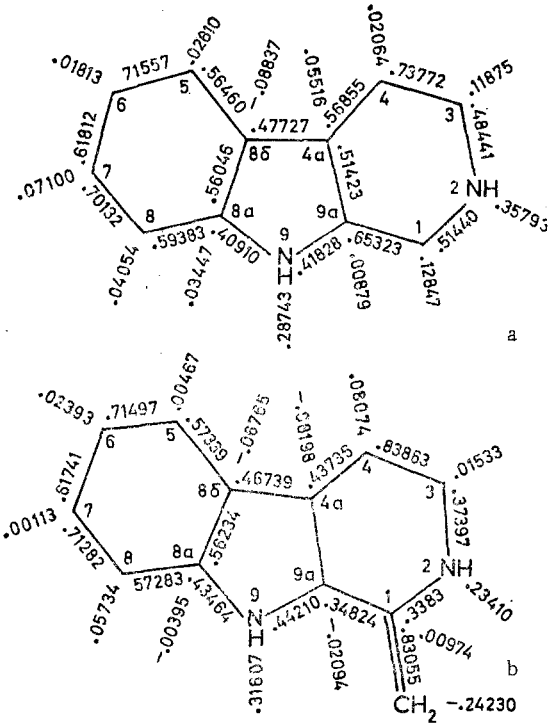
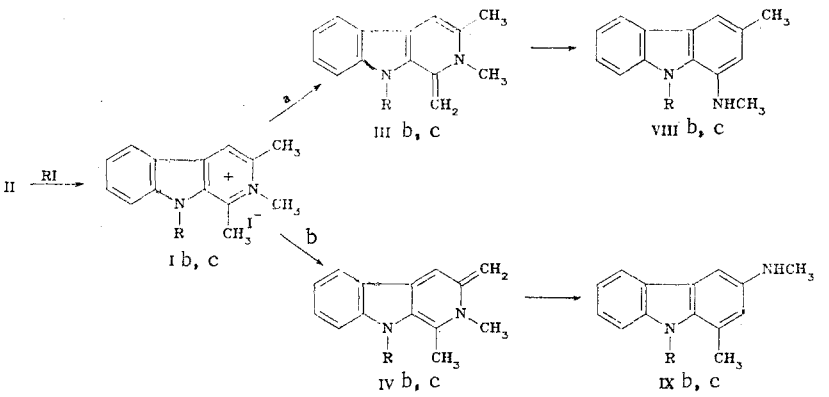
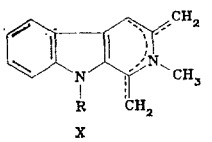


Fig. 1. Molecular diagrams: a) the pyrido[3,4-b]indole cation; b) 1-methylene-9H-1,2-dihydropyrido[3,4-b]indole.



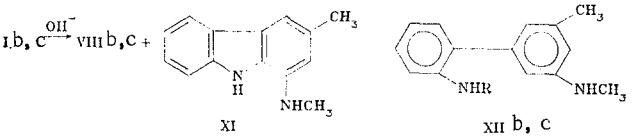
If one excludes the possibility of the formation of anhydro base II from cation I, as, for example, by replacement of the NH group by an N-alkyl group, the reaction of the resulting quaternary salt may proceed via the formation of anhydro bases III and IV, each of which may subsequently undergo opening of the pyridine ring with subsequent ring closure to give a benzene ring, as in the recyclization of 1,2,3-trimethylisoquinolinium iodide [5].

Salts Ib, c may form two anhydro bases of the III and IV type by the action of hydroxide ions on them. The preferableness of the formation of one of them can be evaluated from the π-electron residual charges on the methylene groups in the 1 and 3 positions, as described in [6]. Calculation of anion X shows that the negative π-electron charge on the methylene group in the 3 position is higher in absolute value than that on the methylene group in the 1 position (—0.42384 and —0.38127, respectively):


X

This indicates the higher CH acidity of the methyl group in the 1 position of the ring as compared with that in the 3 position, and the reaction of salts Ib, c with hydroxide ions should therefore be shifted to favor the formation of anhydro bases IIIb, c.

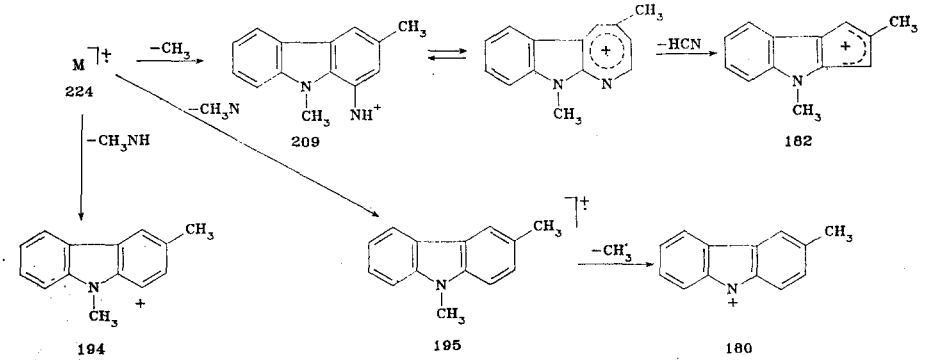
According to the results of the calculations, the weakest bonds in III are the 1–2 and 2–3 bonds (0.3388 and 0.3740, respectively), which may be cleaved during the reaction (see Fig. 1). The residual π-electron charge on the $C_{(3)}$ atom in this compound is positive and is equal to +0.01533, whereas the charge in the 4 position is negative and is equal to −0.08074, i.e., hydroxide ions should attack the C_3 position with cleavage of the 2–3 bond. The formation of a new bond occurs at the 3–10 bond. The order of this bond in III is 0.1212 and is increased with cleavage of the 2–3 bond (the corresponding resonance integral was assumed to be equal to zero) and becomes equal to 0.18369. Electron-donor substituents in the 2 position weaken the 1–2 and 2–3 bonds and increase the long-range order of the 3–10 bond, i.e., they promote recyclization. Substituents in the indole fragment of the molecule have a slight effect on the orders of the bonds undergoing cleavage and the newly formed bonds and, consequently, on the direction of recyclization. Consequently, in the reaction of salts Ib, c with alkali one should expect the preferable formation of VIIIb, c. In addition to this, the recyclization process is supplemented by dealkylation of the indole nitrogen atom, which, in the case of both salt VIIIb and VIIIc, leads to the same compound, viz., carbazole derivative XI. Diaminobiphenyl derivatives XIIb, c, were also isolated in low yields from the reaction mixture. These compounds are formed as a result of recyclization of the pyridinium ring of salts Ib, c with simultaneous cleavage of the C–N bond of the pyrrole ring of the system:



XI XII b, c

Singlet signals at 1.99 and 1.98 ppm, which belong to the methyl groups bonded to the aromatic ring, singlets at 4.14 and 4.13 ppm and at 4.03 and 4.00 ppm, which we assigned to the N-methyl groups, and multiplets of aromatic protons centered at 7.3 and 7.5 ppm are observed in the PMR spectra of VIII and XII. Singlets at 1.99 and 4.14 ppm, which were assigned to the protons of C- and N-methyl groups, are also observed in the PMR spectrum of carbazole XI.

A molecular-ion peak (M^+) at 224,* which corresponds to its molecular mass, was recorded in the mass spectrum of derivative VIIIb. The isotope corrections found correspond to the theoretical values (17.70 and 17.58%) for empirical composition $C_{15}N_{16}N_2$. The tendency of π-surplus hetaryls to undergo ring expansion through the elimination of radicals via a mechanism involving β cleavage relative to the hetaryl ring is known [24]. In fact, the $(M - CH_3)^+$ ion peak at 209 is the second most intense (after M^+) peak [the high W_M value (11.5% [25]) constitutes evidence for the aromatic character of the examined compound]. The obtained direct elimination of NCH_3 (195) and $NHCH_3$ (194) particles from M^+ (proved by recording of the mass spectra of metastable ions) constitutes indirect evidence in favor of the formation of precisely VIIIb rather than IXb (α cleavage due to the "peri" effect). The recording of ion peaks at 167, 166, 152, 140, 139, 77, and 76 in the mass spectrum rigorously proves that the hetaryl belongs to the carbazole system [26]. The indicated pathways of the fragmentation of M^+ are illustrated by the following scheme:



*Here and subsequently, the m/z values are given for the ion peaks.

An M^+ peak at 210, which was the most intense peak (W_M = 12.0%), was recorded in the mass spectrum of carbazole XI. Its fragmentation proceeds with splitting out of hydrogen (209) and a CH_3 radical (195). The subsequent possible expansion of the ring to tropylium and azatropylium rings, respectively, is accompanied by the elimination of CH_3 (194) and HCN (167) particles. The fundamental trend of the fragmentation differs little from the trend examined above for VIIIb (no process due to the "peri" effect occurs). An M^+ peak at 226 was recorded in the mass spectrum of biphenyl XIIb. Its intensity and stability with respect to electron impact (W_M = 3.2%) are considerably lower than in the case of the preceding cyclic structures. The $(M - CH_3)^+$ and $(M - CH_3) - H^+$ (211 and 210) ion peaks have the maximum intensities. The development of the latter ion is associated with the formation of a cation radical with the 1-methylamino-3-methylcarbazole structure. The presence of a bulky ortho substituent suggests that the noncoplanarity of the system as a whole and, as a consequence, the interannular bond undergo destruction to give ions at 106 and 120 under electron impact conditions. The structures of both particles that make up the biphenyl system are monitored in this way. The course of the fragmentation of the ion with the 1-methylamino-3-methylcarbazole structure resembles the processes involved in the dissociative ionization of the systems examined above (ions that are specific for fragmentation of the carbazole ring are present here).

Thus it follows from all of the information set forth above that heteroannelation of the pyridine ring does not hinder rearrangement of the pyridine ring to a benzene ring.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The PMR spectra of solutions in trifluoroacetic acid were recorded with a Tesla-80 spectrometer with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with a Varian MAT 311A spectrometer at an accelerating voltage of 3 kV, a cathode emission current of 300 mA, and an ionizing voltage of 75 kV; the ion-source temperature was 250-300°C. Chromatography in a loose thin layer of activity II (Brockmann scale) aluminum oxide was accomplished by elution with chloroform–benzene–hexane (30:6:1); the chromatograms were developed with iodine vapors and in UV light.

1,2,3-Trimethylpyrido[3,4-b]indole (II). A suspension of 3 g (0.01 mole) of 2,3-dimethyl-9H-pyrido[3,4-b]indole methiodide (I) in 20 ml of a saturated ethanol solution of KOH was refluxed for 1 h, after which the mixture was cooled, and the resulting precipitate was removed by filtration and recrystallized from ethanol to give 1.6 g (86%) of a product with mp 239-240°C. Found: C 80.1; H 6.9; N 13.6%. $C_{14}H_{14}N_2$. Calculated: C 80.0; H 6.7; N 13.3%.

1,3,9-Trimethylpyrido[3,4-b]indole Methiodide (Ib). A mixture of 1.6 g (0.008 mole) of anhydro base II and 1.1 g (0.008 mole) of methyl iodide in 15 ml of ethanol was refluxed for 1 h, and the resulting precipitate was removed by filtration and recrystallized from dimethylformamide (DMF) to give 1.9 g (72%) of product. Found: C 51.0; H 5.1; I 36.4; N 8.1%. $C_{15}H_{17}IN_2$. Calculated: C 51.1; H 4.8; I 36.1; N 8.0%.

1,3-Dimethyl-9-ethylpyrido[3,4-b]indole methiodide (Ic) was similarly obtained in 69% yield by the reaction of the anhydro base with ethyl iodide. Found: C 52.3; H 5.3; I 34.9; N 7.9%. $C_{16}H_{19}IN_2$. Calculated: C 52.5; H 5.2; I 34.7; N 7.7%.

Reaction of 1,3,9-Trimethylpyrido[3,4-b]indole Methiodide (Ib) with Alkali. A suspension of 1 g (0.003 mole) of Ib in 20 ml of a saturated ethanol solution of alkali (KOH) was maintained in a sealed ampul at 100°C for 30 h, after which it was cooled and poured into 100 ml of water. The aqueous mixture was extracted several times with chloroform, and the chloroform extracts were combined, dried with potassium carbonate, and partially evaporated. Hexane was added, and the resulting precipitate was removed by filtration and recrystallized from ethanol to give 0.1 g (17%) of 1-methylamino-3-methylcarbazole (XI) with mp 164-165°C and R_f 0.26. IR spectrum: 3490 (indole NH) and 3300 cm^{-1} (amine NH). PMR spectrum: 1.99 (s, 3H, C–CH_3), 4.14 (s, 3H, N–CH_3), and 6.5-7.8 ppm (m, aromatic protons). Mass spectrum, m/z: 50 (32.6), 55 (15.6), 63 (13.5), 74 (14.5), 77 (24.2), 78 (19.0), 85 (15.6), 139 (6.2), 140 (5.2), 152 (5.1), 166 (6.3), 167 (17.2), 168 (5.6), 180 (8.3), 181 (4.7), 182 (3.4), 194 (11.2), 195 (13.6), 208 (4.1), 209 (61.1), 210 (17.2). Found: C 80.1; H 6.9; N 13.6%. $C_{14}H_{14}N_2$. Calculated: C 80.0; H 6.7; N 13.3%. The filtrate after separation of XI was evaporated, and the residue was dissolved in chloroform and chromatographed with a

column packed with aluminum oxide by elution with chloroform–benzene–hexane (30:6:1) to give 0.23 g (39%) of 1-methylamino-3,9-dimethylcarbazole (VIIIb) with mp 138-139°C (from methanol) and R_f 0.34. IR spectrum: 3290 cm^{-1} (amine NH). PMR spectrum: 1.99 (s, 3H, 3-CH_3), 4.00 (s, 3H, N–CH_3), 4.14 (s, 3H, N–CH_3), and 6.8-7.3 ppm (m, aromatic protons). Mass spectrum, m/z: 50 (32.6), 51 (44.3), 52 (42.8), 55 (15.2), 56 (23.4), 63 (13.4), 74 (14.4), 76 (23.5), 77 (24.2), 78 (19.0), 83 (19.6), 85 (15.8), 139 (5.1), 140 (3.4), 152 (5.2), 166 (6.3), 167 (17.2), 168 (5.5), 180 (8.2), 181 (4.7), 182 (3.4), 194 (11.0), 195 (13.5), 208 (4.0), 209 (1.0), 210 (17.2), 224 (100). Found: C 80.3; H 7.4; N 12.4%. $C_{15}H_{16}N_2$. Calculated: C 80.4; H 7.1; N 12.5%. We also isolated 0.1 g (13.5%) of 2-methylamino-3'-methylamino-5'-methylbiphenyl (XIIb) with mp 131-132°C (from acetonitrile) and R_f 0.73. IR spectrum: 3300 cm^{-1} (amine NH). PMR spectrum: 1.98 (s, 3H, C–CH_3), 4.14 (s, 3H, N–CH_3), 4.03 (s, 3H, N–CH_3), and 6.7-8.0 ppm (m, aromatic protons). Found: 79.3; H 8.1; N 12.7%. $C_{15}H_{16}N_2$. Calculated: C 79.6; H 8.0; N 12.4%.

The reaction of 1,3-dimethyl-9-ethylpyrido[3,4-b]indole methiodide (Ic) with alkali to give 1-methylamino-3-methyl-9-ethylcarbazole (VIIIc) [31% yield, mp 121-122°C (from methanol), and R_f 0.71. Found: C 80.8; H 7.6; N 11.5%. $C_{16}N_{18}N_2$. Calculated: C 80.7; H 7.6; N 11.8%], 1-methylamino-3-methylcarbazole (XI) [15% yield, mp 163-164°C (from methanol); no melting point depression observed for a mixture of this product with a sample obtained by the method described above], and 2-ethylamino-3'-methylamino-5'-methylbiphenyl (XIIc) [12% yield, mp 96-97°C (from hexane), and R_f 0.24. Found: C 80.1; H 8.5; N 11.9%. $C_{16}H_{20}N_2$. Calculated: C 80.0; H 8.3; N 11.7%] also proceeded similarly.

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^{13}C NMR SPECTRA OF 9-METHYLCARBAZOLES AND ELECTRON CONDUCTIVITY OF THE CARBAZOLE RING

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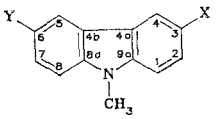
V. P. Lopatinskii, and M. M. Sukhoroslova

UDC 547.759.32

The effect of substituents in the ring of 9-methylcarbazoles on the ^{13}C NMR chemical shifts was determined. Correlation relationships between the inductive and resonance constants of the substituents and the chemical shifts were found. The transmission properties of the carbazole ring with respect to the electronic effects of substituents in the 3 position were evaluated on the basis of the results obtained. Nonadditivity of the effects of the substituents on the NMR chemical shifts within the limits of one phenyl ring of carbazole relative to monosubstituted benzenes was observed.

The chemical shifts in the ^{13}C NMR spectra may serve as a measure of the electron densities on the carbon atoms [1, 2]. We determined the ^{13}C NMR chemical shifts of 9-methylcarbazole (Ia) and a number of 3,6-disubstituted 9-methylcarbazoles (Ib-g) in order to evaluate the degree of transmission of the electronic effects of substituents X and Y through the carbazole ring.



I a-g

I a X=Y=H; b X=CH_3, Y=H; c X=CH_3CO, Y=H; d X=CF_3CO, Y=H; e X=Cl, Y=H; f X=NO_2, Y=H; g X=Y=CH_3CO

To minimize the effect of the solvent the NMR spectra of Ia-g were recorded in a slightly polar solvent ($CDCl_3$) at low concentrations (4% for Ia-e, g and 2% for If). The ^{13}C chemical shifts are presented in Table 1 along with the ^{1}H NMR chemical shifts of the signals of the methyl groups of the same compounds (3% solutions in $CDCl_3$). The assignment of the ^{13}C NMR signals of methylcarbazole Ia and symmetrically substituted derivative Ig on the basis of the previously obtained results from the NMR spectra of 9-alkenylcarbazoles [3] and data on selectively deuterated carbazoles [4] does not present any difficulties. However, the carbon atoms of the two phenylene rings in 3-substituted Ia-f are nonequivalent. Experiments with selective suppression of the spin–spin coupling with the protons were used, the relative intensities of the signals were taken into account, and the obvious assumption that substituents X should have a greater effect on the change in shielding of the nuclei in the substituted ring was made in these cases for assignment of the signals. In addition, the additive constants of substituents X in aromatic compounds [5] were used in the assignment of the chemical shifts of the atoms of the substituted ring.

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