^1H AND ^{13}C NMR SPECTRA OF AND MO CALCULATIONS OF π-ELECTRON DENSITY IN ANGULAR BENZOINDOLES AND PYRROLOQUINOLINES

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In recent years the work of organic chemists engaged in the search for new physiologically active preparations has made condensed heterocyclic compounds such as benzoindoles and pyrroloquinolines available for spectroscopic study [1, 2]. The experimental ^1H and ^{13}C NMR work would make possible the structural verification and a reasonably complete description of the electronic structure of these compounds and would also allow the results of quantum-chemical calculations to be assessed.

The basis of the structures of the compounds in question, 4,5-benzoindole (I), 3H-pyrrolo[3,2-f]quinoline (II), 3H-pyrrolo[2,3-h]quinoline (III), 6,7-benzoindole (IV), 1H-pyrrolo[3,2-h]quinoline (V), and 1H-pyrrolo[2,3-f]quinoline (VI), is indole, with which a benzene or pyridine ring is fused. Consequently, the numbering system of indole can be adopted for these compounds, which seems justifiable [3] for a comparison of spectral and theoretical results for this series of compounds and indole (Fig. 1).

The proton spectra of compounds (I)-(VI) were recorded in CCl_4. We assigned the signals on the basis of our earlier work [3-5], where we made a detailed analysis of the PMR spectra of these compounds in DMSO-d_6 solution. We used the plots of chemical shift against concentration to derive the chemical shifts at infinite dilution, δ_{dil}(X-H) ppm (here and subsequently X = 2, 3, ..., 13), into which we then incorporated a correction for the ring current, δ_{corr}(X-H) ppm. This correction was calculated by an additive scheme using Johnson and Bovey's table [6], assuming that the currents in the five- and six-membered rings are equal. We assumed that these molecules are planar and because of the lack of x-ray data used the same geometrical parameters for the two types of isomers of the 4,5- and 6,7-condensed indole derivatives, those calculated by Dewar [7] for 4,5- and 6,7-benzoindoles, respectively. Table 1 collects all the fundamental experimental results derived for compounds (I)-(VI), including the ^1H chemical shifts, both δ_{dil}(X-H) and δ_{corr}(X-H), and the ^{13}C chemical shifts, δ(X-^{13}C).

Table 1 shows that the 3-H proton appears at highest field in both the 6,7- and the 4,5-condensed indole derivatives. This signal is at higher field in compounds (IV)-(VI) than in (I)-(III) and is less sensitive to the nature of the additional fused ring. The chemical shifts δ_{dil}(X-H) of the 3-H and 2-H protons in indole [8] are closer to those in the 6,7-condensed indole derivatives than in the 4,5-isomers.

We used several methods to assign the ^{13}C signals of compounds (I)-(VI): comparison of the multiplicity of the signals in the ^{13}C single resonance spectra and the systematic variation in the chemical shifts in these compounds and those like indole [9, 10], pyrrole [11], and pyridine [12], partial proton decoupling, and selective proton decoupling. We recorded the ^{13}C NMR spectra of compounds (I)-(VI) in DMSO-d_6 solution. The posssibility of using less polar solvents is limited by the poor solubility of these compounds.

The $C_{(3)}$ signal is at higher field in the 4,5-condensed indole derivatives than in the 6,7-isomers, although the opposite applies to the PMR spectra. Moreover, the $C_{(3)}$ chemical shift in the 4,5-isomers is more sensitive to the nature of the additional fused ring than in the 6,7-isomers. The $C_{(2)}$ chemical shift is less sensitive than the $C_{(3)}$ to the type of ring fusion.

We calculated the basic electronic parameters of compounds (I)-(VI) by the Hückel MO method [13], which in several cases provides reasonably correct estimates of the energy of the molecule and the π-electron density distribution. Alonso et al. [14] made the first calculations of the electronic structure of benzoindole isomers (I) and (IV). They found that in the angular

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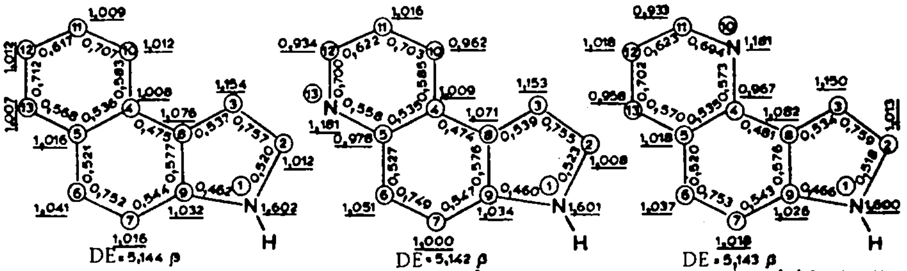
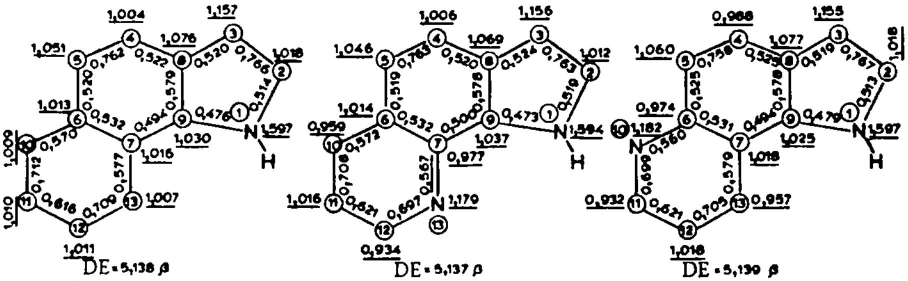


4,5-benzoindole (I) 3H-pyrrolo[3,2-f]quinoline (II) 3H-pyrrolo[2,3-h]quinoline (III)



6,7-benzoindole (IV) 1H-pyrrolo[3,2-h]quinoline (V) 1H-pyrrolo[2,3-f]quinoline

Note. Numbers in circles are the numbers of the atoms; π-charges are underlined, bond orders are not; DE is the delocalization energy (β).

Fig. 1

benzoindole isomers the maximum charge density and the minimum localization energy for electrophilic substitution correspond to position $C_{(3)}$. This is in good agreement with experiment [1]. Dewar et al. have also made calculations in the semiempirical SCF MO π approximation for compounds (I) and (IV) [7], which reveal that the charge on the $C_{(3)}$ atom is the most negative. However, the variations in the π-electron densities on the atoms in these compounds derived by Dewar [7] and Alonso [14] are not the same. This may be due to the simplifications inherent in the Hückel method.

Our calculations were intended to analyze the changes in the electronic properties of the indole fragment with various types of fusion and to assess their agreement with the experimental ^{1}H and ^{13}C NMR results [15]. We used Pullman's [16] or Streitweiser's [13] values for the coulomb and resonance integrals. Since both gave no differences in the relative electron density distribution, we quote only the results of calculations using Pullman's parameters (Fig. 1).

The delocalization energies (DE) for these compounds imply that the energy gain due to annelation is greater for the 6,7-condensed indole derivatives than for the 4,5-isomers.

The molecular diagrams show that the differences in the π-charges on the nonbridgehead carbon atoms of the pyrrole part of the molecule, $\Delta\rho = \rho_3 - \rho_2$, and the bond orders between them, $p_{2,3}$, are lower than in indole. These differences imply that the delocalization of the π-charges of the pyrrole ring is greater in the 4,5- than in the 6,7-isomers.

When comparing the NMR results with the calculated π-electron density distributions we assumed that the effect of the anisotropy of the atoms is constant in this series of compounds and that intermolecular interactions can be neglected.

The variation in ρ_X of the indole fragment correlates adequately with that of the proton chemical shifts corrected for the ring current. The exception is the charges on the atoms in the peri position to which are the nitrogen atoms of the conjugated pyridine ring, i.e., ρ_4 and ρ_5 in compounds (II) and (VI). For the additional fused ring the variation in ρ_X coincides with that in δ_{corr}(X-H) when this ring is pyridine [compounds (II), (III), (V), and (VI)].

Lauterbur [18] introduced an equation relating the ^{13}C chemical shifts to the π-electron densities in nitrogen-containing heterocyclic compounds, like that derived for aromatic compounds by Karplus and Pople [17], by including the σ-polarization charge on the carbon atoms adjacent to the heteroatom:

$$\Delta\sigma_A = 117\Delta q_\pi + 117\Delta q_\sigma + 58\Delta F, \qquad (1)$$

TABLE 1. ^{1}H Chemical Shifts, δ_{dil}(X-H), δ_{corr}(X-H), and ^{13}C Chemical Shifts, δ(X-^{13}C), ppm, in Angular Benzoindoles and Pyrroloquinolines

X	I	II	III	IV	V	VI	Indole
2	(7,13) 6,74 124,29	(7,24) 6,85 125,74	(7,35) 6,96 125,16	(7,16) 6,73 124,31	(7,29) 6,90 125,87	(7,21) 6,82 125,81	(7,08)[8] 125,87
3	(6,97) 6,02 101,95	(7,00) 6,05 102,72	(7,23) 6,28 103,05	(6,58) 5,92 104,03	(6,62) 5,92 104,22	(6,62) 5,92 104,48	(6,45)[8] 102,33
4				(7,59) 6,85 121,84	(7,69) 6,95 122,56	(7,81) 7,07 125,48	121,26
5				(7,40) 6,58 120,67	(7,35) 6,52 119,76	(7,67) 6,85 122,04	120,06
6	(7,46) 6,64 122,90	(7,78) 6,96 123,79	(7,50) 6,68 122,36				122,17
7	(7,38) 6,64 114,82	(7,60) 6,86 118,26	(7,46) 6,72 115,79				112,48
10	(8,11) 7,10 123,92	(8,43) 7,42 132,18		(7,79) 7,05 129,38	(8,15) 7,41 136,86		
11	(7,36) 6,99 126,45	(7,36) 6,99 121,65	(8,80) 8,43 149,73	(7,38) 7,07 126,26	(7,31) 7,00 120,15	(8,73) 8,42 148,37	
12	(7,36) 7,04 123,92	(8,76) 8,44 147,85	(7,27) 6,95 119,89	(7,38) 7,01 124,51	(8,73) 8,36 148,83	(7,31) 6,94 121,58	
13	(7,76) 7,03 129,47		(8,07) 7,34 137,38	(7,88) 6,87 121,71		(8,20) 7,19 130,03	

where $\Delta\sigma_A = (\sigma_A - \sigma_{\text{benzene}})$, $\Delta F = (F_A - F_{\text{benzene}})$, F is the free-valence parameter, and Δq_i is the σ- or π-polarization charge relative to benzene. We have omitted higher-order terms from this equation.

Table 2 summarizes the ^{13}C chemical shift differences, $\Delta\delta(^{13}\text{C}) = \delta(\text{X-}^{13}\text{C}) - \delta(\text{X-}^{13}\text{C}_{\text{indole}})$, with the same X = 2, 3, 4, 5, 6, 7. Here we also quote the changes in the corresponding π-charges and free-valence parameters relative to indole, together with the sum of all the terms of Eq. (1). For these compounds we took the σ-polarization term as constant and equal to its value in indole, i.e., $\Delta q_\sigma = 0$. Table 2 implies that the changes in the calculated values of ρ_X correlate adequately with those in the $C_{(3)}$ and $C_{(4)}$ chemical shifts in the 6,7-derivatives and in the $C_{(2)}$ and $C_{(7)}$ chemical shifts in the 4,5-derivatives. This is a demonstration that the carbon atoms closest to the additional fused ring are most sensitive to the changes introduced by it. The inclusion of the effect of the closest nonadjacent atoms in the MO calculation and of the terms with $\Delta q_\sigma \neq 0$ in Eq. (1) seems to provide better agreement between the calculated and experimental figures.

Use of $\Delta q_\sigma = 0.01$ for the $C_{(2)}$ atoms in compounds (II), (III), (V), and (VI) brings the calculated value into much better agreement with experiment (see the figures in brackets in Table 2).

We have mentioned the high-field position of the $C_{(3)}$ signal in the 4,5-isomers relative to the 6,7-isomers. At first sight the different geometries of these isomers could be responsible for the difference in shielding contributions from the charges on the adjacent nonbonded atoms. However, the calculation revealed that in the 4,5- and 6,7-isomers the electrostatic terms $\Sigma Z_{N'}/R_{NN'}$ [19] are equal, where $R_{NN'}$ is the distance from the N nucleus in question to all the nuclei of the system with charges $Z_{N'}$. The explanation for the behavior of the $C_{(3)}$ signal thus resides in the differences in the conjugated systems of the 4,5- and 6,7-isomers. For compounds (I) and (IV) this also follows from the fluorescence and phosphorescence spectra [20]. In conclusion we should note that Hückel calculations of the π-charges provide better agreement with the experimental NMR than do the Dewar calculations for almost all these compounds [7]. Obviously Dewar's method overestimates the effect of the heteroatom on the carbon atoms adjacent to it.

Thus analysis of the ^{1}H and ^{13}C NMR spectra and comparison of the experimental NMR results and the MO calculations reveal that:

1) in all these compounds the charge on the $C_{(3)}$ atom is the most negative; it is higher in the 6,7- than in the 4,5-isomers;

TABLE 1. Experimental and Calculated [from Eq. (1)] Relative ^{13}C Chemical Shifts in Angular Benzoindoles and Pyrroloquinolines

Compound	Atom	$\rho_X - \rho_{X\,\text{indole}}$	$F_X - F_{X\,\text{indole}}$	$\Delta\sigma_X$	$\Delta\delta_{^{13}C}$
I	C-2	+0,013	+0,005	+1,85	+1,58
	C-3	−0,016	−0,012	−2,54	+0,38
	C-6	+0,010	+0,051	+4,18	−0,73
	C-7	−0,021	0,000	−2,44	−2,34
II	C-2	+0,009	+0,004	+1,31 (+0,14)	+0,31
	C-3	−0,017	−0,012	−2,66	−0,39
	C-6	+0,020	+0,049	+5,20	−1,62
	C-7	−0,036	+0,001	−4,23	−5,78
III	C-2	+0,014	+0,005	+1,92 (+0,75)	+0,71
	C-3	−0,020	−0,011	−2,97	−0,72
	C-6	+0,006	+0,051	+3,65	−0,19
	C-7	−0,019	+0,001	−2,22	−3,31
IV	C-2	+0,019	+0,002	+2,30	+1,56
	C-3	−0,013	−0,004	−1,76	−1,70
	C-4	−0,019	−0,002	−2,34	−0,58
	C-5	+0,012	+0,050	+4,30	−0,61
V	C-2	+0,014	0,000	+1,56 (+0,39)	0,00
	C-3	−0,014	−0,005	−1,97	−1,89
	C-4	−0,017	−0,002	−2,15	−1,30
	C-5	+0,008	+0,049	+3,73	+0,30
VI	C-2	+0,019	+0,002	+2,29 (+1,12)	+0,06
	C-3	−0,015	−0,004	−1,98	−2,15
	C-4	−0,035	−0,002	−4,20	−4,22
	C-5	+0,021	+0,048	+5,23	−1,98

2) the nature of the additional fused ring has a greater effect on the chemical shifts δ_{corr}(3-H) and $\delta(^{13}C_{(3)})$ in the 4,5-isomers than in the 6,7-condensed indole derivatives;

3) the variation in the proton chemical shifts δ_{corr}(X-H) is adequately described by that of the π-charges ρ_X;

4) comparison of the experimental chemical shifts $\delta(^{13}C_{(2)})$ with those calculated with inclusion of the σ-polarization term due to the indole nitrogen atom reveals that Δq_σ is not altered by fusion of a benzene ring, whereas it is reduced by fusion of a pyridine ring;

5) the delocalization of the π-charges of the pyrrole ring is greater in the 4,5- than in the 6,7-condensed indole derivatives.

EXPERIMENTAL

The NMR spectra were recorded on Varian HA-100 and Bruker WH-90 spectrometers. The ^{13}C NMR spectra were recorded with pulse intervals of 1 to 5 sec; the internal standard was C_6D_{12}. All ^1H and ^{13}C chemical shifts were converted to refer to TMS. The MO calculations were carried out with standard programs on BÉSM-6 and Minsk-32 computers.

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BASE-CATALYZED REACTIONS OF QUATERNARY SALTS OF 2- AND 4-AZAFLUORENES

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Armit and Robinson's work [1] on the conversion of 7,8-methylenedioxy-5-methyl-11-phenylindeno[3,2-b]quinolinium monomethyl sulfate when treated with aqueous alcoholic potassium hydroxide to 7,8-methylenedioxy-5-methyl-11-phenyl-5H-indeno[3,2-b]quinoline was one of the sources of the chemistry of pseudoazulenes [2], isoelectronic analogs of azulene, for whose structure a mesomeric form with Kekulé and dipolar structures has been suggested [1, 3].

The isomeric azafluorenes are of particular interest for the synthesis of pseudoazulenes. Treibs and Beger [3] have theoretically examined N-alkyl-substituted 1H(2H,3H,4H)-indenopyridines, which correspond to the four isomeric azafluorenes. However, since the discovery of pseudoazulenes only one compound of this type has been prepared from azafluorenes — 1,2,3-trimethyl-9-phenyl-2H-indeno[2,1-c]pyridine (black acicular crystals with mp 212-216°C) [4]. The lack of simple methods for the synthesis of azafluorenes has retarded the development of this area of the chemistry of nitrogen heterocycles.

Azafluorenes are also of interest for the synthesis of azafluorenium ylides. The chemistry of pyridinium ylides has now been thoroughly studied [5]. However, little is known of the chemistry of azafluorenium ylides. Quaternary salts of azafluorenes are converted under alkaline conditions to azafluorenium ylides and nitrogen-containing pseudoazulenes. Whether compounds of the first or second type are formed depends on the nature of the cation, which is involved in the formation of the quaternary salt.

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