Sg-2 spectrometer with direct introduction of the samples into the ion source at 140-160°C. The temperature of the ionization chamber was 130°C, the ionizing voltages were 75 and 15 V, and the emission current was 250 μA.

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# CALCULATION OF THE PHYSICOCHEMICAL PROPERTIES OF THIENOPYRIDINES BY THE PARISER—PARR—POPLE (PPP) METHOD

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The dipole moments, diamagnetic susceptibilities, chemical shifts of the $^{1}H$, $^{13}C$, and $^{14}N$ nuclei, and the energies of the lowest singlet—singlet transitions of aza-substituted thiophenes and benzo[b]thiophenes were calculated within the framework of the bonded variant of perturbation theory by the Pariser—Parr—Pople (PPP) method. A scale of aromatic character of the investigated class of compounds is given on the basis of the current distributions found.

Thienopyridines, like other structures similar to them, are of substantial theoretical interest, since π-surplus (the thiophene ring) and π-deficient (the pyridine ring) fragments are united in one molecule [1]. In addition, they are also of interest for pharmacology because of the high physiological activity of some derivatives of this series [2]. A method for taking into account the d orbitals of the sulfur atom in describing the electronic structures and physicochemical characteristics of sulfur-containing heterocycles was previously developed [3] within the π-electron approximation of the MO LCAO SCF method on the basis of the Longuet—Higgins model. In the present paper it is used to calculate the dipole moments, energies of the lowest singlet—singlet transitions, diamagnetic susceptibilities, and chemical shifts of the $^{1}H$, $^{13}C$, and $^{14}N$ nuclei of a number of thienopyridines.

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TABLE 1. Dipole Moments (μ, D), Energies of the Lowest Singlet—Singlet Transitions (E, eV), Induced π-Electron Ring Currents (I, in units of benzene current), and Diamagnetic Susceptibilities [relative to benzene ($\chi^I$) and molar diamagnetic susceptibilities ($\chi_M$), in units of $10^6$ cm³/mole]

| Compound | Name | $\mu^\pi$ | μ |  | $E_1$ |  | $E_2$ |  | $I_1$ | $I_2$ | $\chi^I$ | $-\chi_M$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | calc. | exptl. | calc. | exptl. | calc. | exptl. |  |  |  |  |
| I | Thiophene | 0,86 | 0,63 | 0,55 | 5,26 | 5,16 | 6,49 | 6,59 | 0,848 | — | 0.664 | 56,40 |
| II | Isothiazole | 1,12 | 2,65 | 2,4±0,2 | 5,11 | 5,08 | 6,26 | — | 0,621 | — | 0,486 | 48,46 |
| III | Thiazole | 1,59 | 1,57 | 1,61 | 5,86 | 5,80 | 6,57 | — | 0,902 | — | 0,712 | 50.80 |
| IV | Benzo[b]thiophene | 0.81 | 0,72 | 0,62 | 4,11 | 4,19 | 4,56 | 4,68 | 0,910 | 1,068 | 1,779 | 93.26 |
| V | Benz[d]isothiazole | 0,89 | 3,26 | — | 3,97 | — | 5,02 | — | 0,608 | 1,068 | 1,506 | 85,09 |
| VI | Benzo[d]thiazole | 1,53 | 1,35 | 1,32 | 4,19 | 4,27 | 4,93 | 4,84 | 0,971 | 1,076 | 1,834 | 88,50 |
| VII | Thieno[3,2-b]pyridine | 1,65 | 1,63 | — | 4,10 | 3,94 | 6,00 | 5,39 | 0,906 | 1,071 | 1,778 | 87,92 |
| VIII | Thieno[3,2-c]pyridine | 1.52 | 1,86 | 2,15 | 4,15 | 4.23 | 5,07 | 5.56 | 0,909 | 1.068 | 1,778 | 87,92 |
| IX | Thieno[2,3-c]pyridine | 1,45 | 2,52 | 2,61 | 4,10 | 4,06 | 4,62 | 4,82 | 0,910 | 1.071 | 1,781 | 87,95 |
| X | Thieno[2,c-b]pyridine | 0,39 | 3,02 | — | 4,10 | — | 5,55 | — | 0,905 | 1,069 | 1,775 | 87,89 |

The results of calculation by the method in [3] of the dipole moments of aza derivatives of thiophene and benzo[b]thiophene are presented in Table 1. It is apparent from Table 1 that the calculation describes the available experimental data quite well [2, 4]; the maximum values of the dipole moments correspond to compounds in which the σ contributions to the total dipole moment, which are related to the nitrogen and sulfur atoms, are directed to the same side. These are generally molecules with closely situated heteroatoms. The π-electron contribution to the dipole moments is minimal for thieno[2,3-b]pyridine (X) and maximal for thieno[3,2-b]pyridine (VII), while the situation is reversed for the total dipole moments in the thienopyridine series.

The energies of the lowest singlet—singlet transitions (Table 1) were determined as the eigenvalues of the stability matrix of the Hartree—Fock ground state [5], and in this sense the accuracy of the description of the excited states corresponds to the level of approximation of the ground state. It is apparent that, in contrast to thiophene, aza substitution in benzo[b]thiophene has little effect on the position of the long-wave band but leads to a 0.06 to 1.44 eV (from ~10 to 60 nm) short-wave shift of the second band. From this, according to [6], it follows that the changes in the charges in the benzo[b]thiophene (IV) molecule when it is excited to the lowest singlet state should be insignificant, while they will change more substantially on passing to the second state. This conclusion is confirmed by calculations of the electron densities of the corresponding excited states of benzo[b]thiophene. Thus in the $S_1$ state the Δq* values change from —0.016 to 0.014, whereas in the $S_2$ state they change from —0.005 to 0.043; the maximum Δq* values correspond to the greatest spectral shifts. Comparing the data in Table 1 with the energies of the lowest singlet transitions of isoelectronic analogs of thienopyridines, viz., quinoline and isoquinoline, calculated by the same method [7], one can see that replacement of the —CH═CH— fragment by a sulfur atom leads to intensification of the effect of aza substitution on the long-wave transitions.

A comparison of the induced ring currents in the five-membered ($I_1$) and six-membered ($I_2$) rings of thienopyridine molecules presented in Table 1 and the analogous values calculated for quinoline ($I_1$ = 1.083, $I_2$ = 1.084), isoquinoline ($I_1$ = 1.085, $I_2$ = 1.086), and naphthalene (I = 1.086) (here $I_2$ is the current in the pyridine ring) shows that replacement of the —CH= grouping by a nitrogen atom (aza substitution) in the benzene ring virtually does not change the current distributions. On the one hand, this makes it possible (see below) to use the current distributions of benzo[b]thiophene, naphthalene, and other arenes in calculations of the magnetic shielding in the corresponding aza-substituted compounds and, on the other, it is a prerequisite in applying perturbation theory in the description of aza substitution.

The calculated (on the basis of the ring currents) relative π-electron contributions to diamagnetic susceptibility $\chi^I = \chi^\pi/\chi_{C_6H_6}{}^\pi$, which are among the indexes of aromatic character (for example, see [8]), and the calculated (by the method in [3, 7]) average values of the tensor of diamagnetic susceptibility $\chi_M$ are also presented in Table 1. Let us immediately note that the calculated $\chi_M$ values correspond to the experimental values: 57.4 ± 0.9·($-10^{-6}$ cm³/mole) for thiophene (I) and 50.6·($-10^{-6}$ cm³/mole) for thiazole (III) [9]. It follows from Table 1 that aza substitution in the five-membered ring of benzo[b]thiophene has a stronger effect than aza substitution in the benzene ring on both the relative diamagnetic suscepti-

TABLE 2. Chemical Shifts of the Protons of Benzo[b]thiophene and Its Aza Derivatives (δ, ppm)

| Compound | Proton | Calc. | | Exptl. | |
|---|---|---|---|---|---|
| | | direct | from perturbation theory | | |
| IV | 2-H | 7,51 | — | 7,31 [12] | 7,40 [13] |
| | 3-H | 7,08 | — | 7,21 | 7,29 |
| | 4-H | 7,43 | — | 7,68 | 7,78 |
| | 5-H | 7,20 | — | 7,24 | 7,33 |
| | 6-H | 7,20 | — | 7,22 | 7,31 |
| | 7-H | 7,88 | — | 7,73 | 7,86 |
| VI | 2-H | 9,31 | 9,23 | 9,23 [14] | |
| | 4-H | 7,94 | 7,92 | 8,23 | |
| | 5-H | 7,23 | 7,23 | 7,55 | |
| | 6-H | 7,20 | 7,20 | 7,55 | |
| | 7-H | 7,91 | 7,89 | 8,12 | |
| VII | 2-H | 7,59 | 7,54 | 7,62 [15] | |
| | 3-H | 7,59 | 7,56 | 7,51 | |
| | 5-H | 8,65 | 8,83 | 8,64 | |
| | 6-H | 7,25 | 7,23 | 7,12 | |
| | 7-H | 7,97 | 7,96 | 8,08 | |
| VIII | 2-H | 7,59 | 7,51 | 7,47 [16] | 7,52 [17] |
| | 3-H | 7,17 | 7,12 | 7,43 | 7,52 |
| | 4-H | 8,87 | 9.06 | 9,11 | 9,21 |
| | 6-H | 8,60 | 8,71 | 8,43 | 8,53 |
| | 7-H | 7,74 | 7,89 | 7,28 | 7,85 |
| IX | 2-H | 7,61 | 7,56 | 7,60 [18] | 7,63 [19] |
| | 3-H | 7,16 | 7,09 | 7,26 | 7,22 |
| | 4-H | 7,43 | 7,43 | 7,56 | 7,57 |
| | 5-H | 8,60 | 8,71 | 8,42 | 8,44 |
| | 7-H | 9,37 | 9,41 | 9,06 | 9,12 |
| X | 2-H | 7,53 | 7,51 | 7,40 [3] | |
| | 3-H | 7,09 | 7,10 | 7,08 | |
| | 4-H | 7,42 | 7,61 | 7,85 | |
| | 5-H | 7,27 | 7,23 | 7,10 | |
| | 6-H | 8,40 | 8,83 | 8,46 | |

bility and the ring π-electron currents (see Table 1); the introduction of a nitrogen atom into the α position with respect to the sulfur atom decreases the diamagnetic susceptibility and the induced ring currents in both the five- and, as a rule, six-membered rings, whereas its introduction into the Δ position has the opposite effect. A similar change in the diamagnetic susceptibility and ring π-electron currents is also observed in the case of aza substitution of the thiophene molecule. This in turn is associated with a decrease in resonance integral $\beta_{N-S} = 1.622$ eV $< \beta_{C-S} = 2.92$ eV; this automatically (see [10, 11]) leads to a decrease in $I_1$.

Since the relative π-electron diamagnetic susceptibilities $\chi^I$ are among the quantitative criteria of aromatic character, it is therefore not difficult to construct a scale of aromatic character of the compounds of the investigated series from the results of the calculation. In conformity with what was stated above, benzisothiazole V turns out to the least aromatic of the aza derivatives of benzo[b]thiophene, while benzo[b]thiophene (IV) and the four thienopyridines have virtually identical aromatic character, and benzothiazole VI has the maximum aromatic character. By comparing the $\chi^I$ values with the analogous values for azines [7], azoles [11], sulfur-containing heterocycles [3], etc., one can easily determine the place that thienopyridines occupy in the general scale of aromatic character of heterocyclic compounds.

A knowledge of the current and charge distributions of the investigated molecules makes it possible, on the basis of a previously developed method [10, 11], to calculate the proton chemical shifts (CS), which are presented in Table 2. As in [3, 7, 10, 11], the contributions of the σ skeleton to magnetic shielding were described on the basis of an additive scheme. It is apparent from the data presented that the calculations, on the whole, correctly reflect the sequence of the signals of the protons both of each individual molecule and in the series of investigated compounds. The experimental data were taken from [2, 12-19].

As noted above, the effect of aza substitution on the physicochemical molecular characteristics can be described on the basis of perturbation theory (see [20, 21]). Thus one can readily calculate chemical shift $\delta_i$ in a substituted molecule if one knows the analogous value for the unsubstituted system $\delta_i{}^0$ and the $\Delta\alpha_R$ value, which characterizes the substituent, from the formula

$$\delta_i = \delta_i{}^0 + \sum_j K_{ij} \Delta\alpha_{R_j} .$$

TABLE 3. Coefficients $K_{ij}$ (ppm/eV) of the Effect of Substituents on the Magnetic Shielding of the Protons in Benzo[b]thiophene (IV)

| Position | 2-H | 3-H | 4-H | 5-H | 6-H | 7-H |
|---|---|---|---|---|---|---|
| 2 | — | 0,261 | 0,045 | 0,007 | 0,038 | 0,011 |
| 3 | 0,272 | — | −0,004 | 0,024 | 0,001 | 0,011 |
| 4 | 0,035 | 0,000 | — | 0,198 | 0,020 | 0,135 |
| 5 | 0,002 | 0,034 | 0,203 | — | 0,111 | 0,005 |
| 6 | 0,041 | 0,008 | 0,003 | 0,110 | — | 0,200 |
| 7 | 0,000 | 0,014 | 0,135 | 0,021 | 0,197 | — |

TABLE 4. Calculated $^{13}C$ Chemical Shifts of Thiophene, Benzo[b]thiophene, and Their Aza-Substituted Analogs (δ, ppm)*

| Compound | 2-C | 3-C | 4-C | 5-C | 6-C | 7-C | 3a-C | 7a-C |
|---|---|---|---|---|---|---|---|---|
| I | 121,9 | 123.5 | — | — | — | — | — | — |
|  | (125,6) | (127,5) | — | — | — | — | — | — |
| II | — | 154,5 | 122,4 | 133,5 | — | — | — | — |
|  | — | (157,0) | (123,4) | (147,8) | — | — | — | — |
| III | 146,7 | — | 145,0 | 120,7 | — | — | — | — |
|  | (153,6) | — | (143,3) | (119,6) | — | — | — | — |
| IV | 124,0 | 123,6 | 126,6 | 125,5 | 125,7 | 125,3 | 130,3 | 129,0 |
|  | (126,4) | (124,0) | (123,8) | (124,3) | (124,4) | (122,6) | (139,9) | (139,8) |
| V | — | 158,0 | 128,5 | 124,6 | 127,7 | 124,6 | 130,1 | 136,4 |
|  | — | (146,4) | (123,1) | (124,7) | (129,2) | (122,1) | (135,4) | (162,2) |
| VI | 149,7 | — | 126,7 | 126,0 | 125,0 | 125,2 | 147,4 | 128,6 |
|  | (155,1) | — | (124,0) | (126,6) | (126,0) | (122,6) | (154,2) | (134,5) |
| VII | 124,9 | 124,0 | — | 150,9 | 124,6 | 131,7 | 149,2 | 128,4 |
| VIII | 123,2 | 124,8 | 152,1 | — | 146,6 | 123,9 | 129,5 | 132,4 |
| IX | 125,2 | 123,3 | 125,2 | 146,4 | — | 150,7 | 133,4 | 138,3 |
| X | 123,1 | 123,8 | 133,0 | 124,4 | 151,1 | — | 129,5 | 148,5 |

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*The experimental values are given in parentheses [14, 25, 26].

The results of calculation of the chemical shifts of the protons with $\Delta\alpha_N = 1.30$ eV [22] are presented in Table 2. The corresponding transmission coefficients $K_{ij}$ (see [21]) are presented in Table 3, and the contributions to proton magnetic shielding due to the currents of the unshared pairs of the nitrogen atoms (as in the "direct" calculation) were taken into account additively (see [22]).

It is apparent that the results of "direct" calculation are satisfactorily reproduced on the basis of perturbation theory. This makes it possible, by calculating only the parent molecule, to describe the properties of the entire examined class of compounds (see [22]), as well as the chemical shifts of functionally substituted benzo[b]thiophenes. Thus replacement of the CH= groups in the conjugated system by a nitrogen atom of the "pyridine" type can be described within the framework of perturbation theory not only for carbocyclic compounds [21] and nitrogen heterocycles [22] but also for sulfur-containing aromatic heterosystems.

On the basis of the current and charge distributions found one can calculate the chemical shifts of both the protons and the nuclei that differ from them (for example, see [2, 23, 24]). An analysis of the π-electron contributions to the magnetic shielding of $^{13}C$ nuclei in series of aromatic carbo- and heterocycles (see [23, 24]) showed that in this case the determining factor is the π-electron charge on the atom under consideration, and the contributions of other residual π-electron charges and, as noted above, the differences in the current contributions due to aza substitution can be disregarded. This makes it possible to dispense with finding the current distributions, which constitutes the burden of the calculation, and to calculate the chemical shifts of the $^{13}C$ nuclei only on the basis of calculation of the π-electron charges of aza-substituted compounds. The results of this sort of calculation are presented in Table 4. For comparison, let us point out that the $^{13}C$ chemical shifts calculated with allowance for all of the contributions are 146.5 $[C_{(2)}]$, 144.8 $[C_{(4)}]$, and 120.8 ppm $[C_{(5)}]$ for thiazole III, 149.3 $[C_{(2)}]$, 126.6 $[C_{(4)}]$, 126.0 (5-H), 125.0 $[C_{(6)}]$, 125.2 $[C_{(7)}]$, 146.8 $[C_{(3a)}]$, and 128.5 ppm $[C_{(7a)}]$ for benzo d thiazole (VI), and so on, i.e., the data in Table 4 virtually do not differ from the results of complete calculation. In addition, this conclusion serves as a foundation for obtaining, from the experimental $^{13}C$ chemical shifts,

TABLE 5. Residual π-Electron Charges ($q^\pi$) and Chemical Shifts of the Nitrogen Nuclei ($\delta$, ppm)

| Compound | $q^\pi$ | Calc. | Exptl. | Compound | $q^\pi$ | Calc. | Exptl. |
|---|---|---|---|---|---|---|---|
| Pyridine | −0,177 | 312 | 318±0,4 | Pyrrole | 0,371 | 143 | 144,6 |
| Pyridazine | −0,087 | 385 | 396 | Indole | 0,327 | 108 | 122,4 |
| Pyrimidine | −0,185 | 305 | 290,6 | Carbazole | 0,287 | 75 | 98±8 |
| Pyrazine | −0,148 | 335 | 332±1 | Indolizine | 0,468 | 222 | 184,8 |
| Acridine | −0,203 | 290 | 282±8 | Imidazole (NH) | 0,379 | 150 | 158} 200 |
| Oxazole | −0,251 | 251 | 249±1 | (N) | −0,262 | 242 | 267} |
| Benzoxazole | −0,275 | 232 | 234±2 | Benzimidazole (NH) | 0,286 | 74 | 139 |
| Oxadiazole | −0,197 | 295 | 294±1 | (N) | −0,255 | 248 | 248 |
| Imidazole anion | −0,279 | 229 | 229±3 | 1-Azaindolizine (NH) | 0,433 | 194 | 194±1 |
| II | −0,230 | 269 | 294±1 | (N) | −0,241 | 259 | 241±2 |
| III | −0,188 | 303 | 320±1 | 2-Azaindolizine (NH) | 0,423 | 186 | 185±1 |
| V | −0,215 | 281 | 300±3 | (N) | −0,211 | 284 | 234±5 |
| VI | −0,173 | 315 | 314±2 | Porphine (NH) | 0,335 | 114 | 137 |
| Ben[c]isothiazole | −0,263 | 242 | 255±2 | (N) | −0,353 | 168 | 244 |
| Quinoline | −0,186 | 304 | 312±0,5 | | | | |
| Isoquinoline | −0,177 | 312 | 308±4 | Cations | | | |
| Quinoxaline | −0,149 | 334 | 330±3 | | | | |
| VII | −0,183 | 307 | — | Pyridinium | 0,367 | 200 | 197 |
| VIII | −0,179 | 310 | — | Quinolinium | 0,330 | 170 | 183±0,5 |
| IX | −0,179 | 310 | — | Isoquinolinium | 0,360 | 194 | 188±2 |
| X | −0,192 | 299 | — | Thieno[3,2-b]pyridinium | 0,333 | 172 | — |
| | | | | Thieno[3,2-c]pyridinium | 0,363 | 197 | — |
| | | | | Thieno[2,3-c]pyridinium | 0,358 | 193 | — |
| | | | | Thieno[2,3-b]pyridinium | 0,332 | 172 | — |

information regarding the change in the charge distribution in a molecule when a —CH= fragment in it is replaced by a nitrogen atom. It also follows from Table 4 that the calculation, on the whole, correctly reflects the regularities in the $^{13}C$ NMR spectra of aza derivatives of thiophene and benzo[b]thiophene.

The dependence of the chemical shifts on the residual π-electron charges on the nuclei being shielded is manifested even more distinctly when one examines the magnetic shielding of $^{14}N$ nuclei (see [24]). In this case one can disregard the contributions of not only adjacent charges but also of the ring currents. It follows from the calculation that the ring contributions to the $^{14}N$ chemical shifts range from 1.5 to 6.5 ppm, while the contributions of adjacent π-electron charges change to an even lesser extent, viz., from −2.2 to 0.8 ppm; at the same time, the chemical shifts of the nitrogen nuclei for azines and azoles range from 100-400 ppm. Thus the magnetic shielding of the $^{14}N$ nuclei in molecules with conjugated bonds can be described on the basis of the residual π-electron charges on the nitrogen atoms being shielded. Such correlations have often been noted by experimenters [27, 28]. In the present research, on the basis of calculation of the charge distributions of a number of five- and six-membered nitrogen heterocycles describable within the framework of a unified theoretical approach and the parameters of a π-electron Hamiltonian we calculated the chemical shifts of a number of azoles, azines, and their cations, which are compared with the experimental values [26-29] in Table 5. We obtained the following correlation dependence for the chemical shifts of the nitrogen nuclei of the pyridine type:

$$\delta_N = (456 \pm 11) + (815 \pm 54) q^\pi$$
$$(r = 0.975; \quad s = 7.94 \text{ ppm}).$$

The slope of this regression is close to that found in [27, 28]. For pyrrole nitrogen atoms calculation at a fixed slope gives a value of the free term $A(\ddot{N}) = -159$ ppm. The effect of the gegenion and solvation on the $^{14}N$ chemical shifts of the cations of nitrogen-containing heterocycles can be taken into account by changing this value to $A(\overset{+}{N}) = -93$ ppm. On the whole, the calculation correctly reflects the available experimental data from $^{14}N$ NMR spectroscopy.

In conclusion, let us note that the good agreement between the calculated physicochemical characteristics of thienopyridines and the experimental values indicates the reliability of the current and charge distributions obtained. The latter, in general, are close to those presented in a review [2] and correctly reflect the reactivity of the investigated class of compounds.

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