

ELECTRONIC STRUCTURES AND REACTIVITIES OF METHYL-SUBSTITUTED THIENOTHIAZOLES
AND THIENO- AND FUROPYRIDINES

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The electronic structures of a number of methyl-substituted heterocycles containing a thiophene or furan ring condensed with a thiazole or pyridine ring and of their quaternary salts and methylene bases were calculated by the Pariser-Parr-Pople method. The features of the electronic structures of the investigated molecules were ascertained. It is shown that methyl-substituted thiethiazoles and thieno- and furopyridines and their quaternary salts are appreciably inferior to the corresponding benzothiazoles and quinoline derivatives used for the synthesis of polymethine dyes with respect to the reactivity of the methyl group.

Methyl-substituted heterocycles with a condensed thiophene or furan ring are of interest as starting materials for the synthesis of polymethine dyes — spectral sensitizers of photographic materials. Data on their electronic structures are extremely necessary for the interpretation and prediction of their different properties. In the present research we investigated the electronic structures and reactivities of a number of methyl-substituted thiethiazoles and thieno- and furopyridines and their quaternary salts and methylene bases.

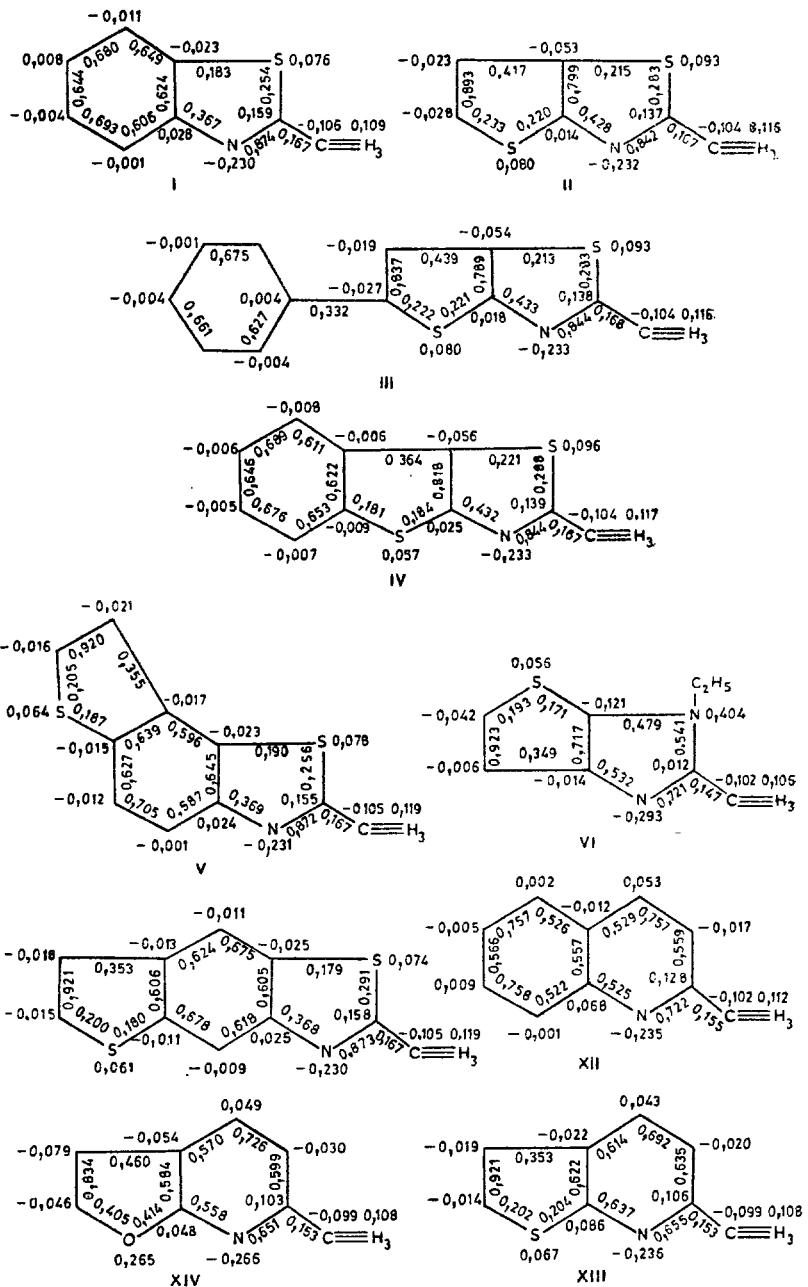
The calculations of the electronic structures were made by the Pariser-Parr-Pople (PPP) method with a program composed by one of us. The $\gamma_{\mu\nu}$ integrals were calculated from the Mataga-Nishimoto formula [1]. The $\beta_{\mu\nu}$ resonance integrals were calculated within the "variable β " approximation [2, 3]. The principal parameters and the details of the calculations are in conformity with those in [4]. The parameters for nitrogen ($W_{\mu} = -28.71$ eV, $\gamma_{\mu\mu} = 16.75$ eV) were determined from the tables of Hinze and Jaffe [5] by the Pariser-Parr procedure [6]. The $\beta_{\mu\nu}$ variation constants for the C-S bond and the W_{μ} and $\gamma_{\mu\mu}$ values of the S atom were borrowed from [7]. The Mulliken hyperconjugation model was adopted for the methyl group. The parameters for it were taken from [8], and the resonance integrals of the C-CH₃ and C≡H₃ bonds remained constant during the calculation.

All of the rings were considered to be regular polygons with bond lengths of 1.40 Å. The exocyclic bonds were directed along the bisectors of the corresponding external angles and were 1.48 Å for C-C and 1.36 Å for the C=C bonds. In conformity with [8], the C-CH₃ and bond lengths were selected to be 1.51 and 0.45 Å.

The results of the calculation (see the diagrams for I-IV and XII-XVI) show that all of the investigated methyl-substituted heterocycles are characterized by a nonuniform distribution of the π -electron density and consequently by considerable nonequivalence of the different positions with respect to different substituents. Thus, replacement of the hydrogen atoms of the condensed thiophene or furan ring in two-ring thiethiazoles, thieno- and furopyridines, and three-ring methylthienobenzothiazoles should be realized most easily by electrophilic reagents. This is in agreement with the experimental data [9, 10]. Electrophilic reagents will also most readily enter into substitution in the three-ring 2-methylbenzothieno [2,3-d]thiazole, and they will replace only the hydrogen atoms of the benzene ring.

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The carbon atoms in the 2 position of the thiazole ring and the α position of the pyridine ring are positively charged in all of the examined compounds. It is known [11, 12] that in the case of α -methyl-substituted azoles, the higher the position π -electron charge on the carbon to which the methyl group is bonded, the higher the order of its bond with the adjacent nitrogen atom, and the hydrogen atoms in this methyl group should be especially labile. Let us examine these characteristics in greater detail.

The investigated methyl-substituted heterocycles can be arranged in the following orders with respect to increasing positive charge:

Pyridine bases: 6-methylfuropyridine < 6-methylthienopyridine < quinaldine; thiazole bases: 2-methylthienothiazole < 2-methyl-5-phenylthienothiazoles < 2-methylbenzo-thienothiazole < 2-methylthieno[2,3-g]benzothiazole < 2-methylthieno[2,3-f]benzothi-azole < 2-methylbenzothiazole.

TABLE 1. Energy Characteristics of the Heterocycles

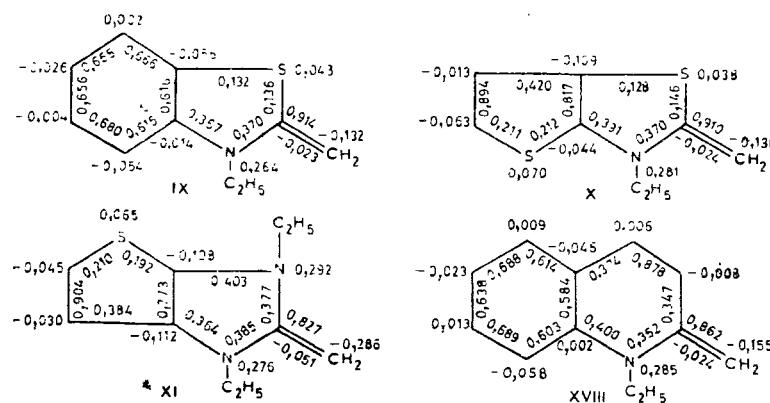
Compound	Name	$-\Delta E_{\pi}^{\text{tot}}$	$-\Delta E_{\pi\alpha}$	$\Delta E^*_{\pi_2}$	$+\delta C_2$ or $+\delta C_6^*$
I	2-Methylbenzothiazole	400,422	17,249	—	—
II	2-Methylthieno[2,3-d]thiazole	407,983	15,280	—	—
III	2-Methyl-5-phenylthieno[2,3-d]thiazole	710,256	22,852	—	—
IV	2-Methylbenzothieno[2,3-d]thiazole	616,937	20,198	—	—
V	2-Methylthieno[2,3-g]benzothiazole	615,302	20,039	—	—
VI	1-Ethyl-2-methylthieno[3,2-d]imidazole	423,332	15,981	—	—
VII	2-Methyl-3-ethylbenzothiazolium	423,664	23,363	10,393	0.615
VIII	2-Methyl-3-ethylthieno[2,3-d]thiazolium	431,306	19,403	10,456	0.571
IX	2-Methylene-3-ethylbenzothiazoline	419,743	12,970	—	—
X	2-Methylene-3-ethylthieno[2,3-d]thiazoline	428,212	8,947	—	—
XI	1,3-Diethyl-2-methylenethieno[2,3-d]imidazoline	441,741	10,699	—	—
XII	Quinaldine	390,745	20,815	—	—
XIII	6-Methylthieno[2,3-b]pyridine	398,796	17,147	—	—
XIV	6-Methylfuro[2,3-b]pyridine	423,184	19,289	—	—
XV	1-Ethyl-2-methylquinolinium	414,047	27,072	11,086	0.446
XVI	6-Methyl-7-ethylthieno[2,3-b]pyridinium	422,123	233,423	11,366	0.393
XVII	6-Methyl-7-ethylfuro[2,3-b]pyridinium	446,637	25,759	13,704	0.391
XVIII	1-Ethyl-2-methylene-1,2-dihydroquinoline	409,584	15,992	—	—
XIX	6-Methylene-7-ethyl-6,7-dihydrothieno[2,3-b]pyridine	418,262	12,056	—	—
XX	6-Methylene-7-ethyl-6,7-dihydrofuro[2,3-b]pyridine	442,888	14,144	—	—

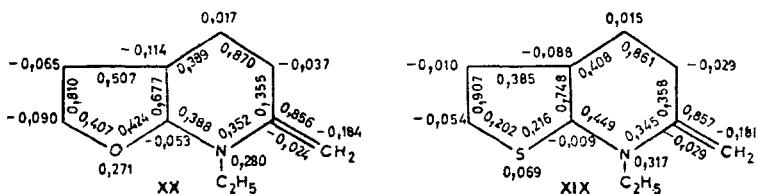
* $\Delta E_{\pi_2} = E_{\pi}$ of the salt $- E_{\pi}$ of the methylene base [13].

† qC_6 for the quaternary salt of 6-methylthieno- and 6-methyl-furopyrindine.

On the whole, a lower positive charge on the carbon in the α position as compared with the corresponding charge in 2-methylbenzothiazole and quinaldine is characteristic for furo- and thieno-containing compounds. In addition, since the azole rings of furo- and thieno-containing compounds have greater leveled character of the bond orders, i.e., they are more aromatic, the orders of the N-C double bonds in them are lower. Consequently, the hydrogen atoms of the α -methyl groups of the thiazole and pyridine rings of such compounds should be less labile.

A comparison of the molecular diagrams of the three-ring compounds shows that the methyl groups in the 2 position of the thiazole ring condensed with benzo[b]thiophene are inferior, with respect to the lability of the hydrogen atoms, to compounds in which the thiophene ring is condensed directly with the benzene ring, i.e., methylthienobenzothiazoles. The introduction of a phenyl group in the 5 position in 2-methylthieno[2,3-d]thiazole leads to a slight increase in the positive charge on C_2 of the thiazole ring and the C=N bond order and, consequently, to a small increase in the lability of the hydrogen atoms of the methyl groups. Methyl-substituted thienoimidazole has the lowest reactivity of the compounds examined in this study.





It is apparent from the results of calculations of the quaternary salts of the investigated compounds (VII, VIII, XV, XVI, and XVII, Table 1) that they also have lower positive charge on the carbon in the 2 position of the thiazole ring and the α position of the pyridine ring than quinaldine and 2-methylbenzothiazole salts. The character of the change in the magnitude of this charge is the same as that observed in the case of the neutral molecules. Thus, by comparing the q_r and $P_{N=C}$ values one can conclude that replacement of the annealed benzene ring by a furan or thiophene ring in the quaternary salts leads to a decrease in the activity of the hydrogen atoms of the methyl groups.

The reactivities of the methyl groups in the quaternary salts can be characterized not only by the magnitude of the π -electron charge on the carbon atom to which the methyl group is bonded and the $N=C$ bond order but also by the magnitude of the delocalization energy (ΔE_{π_2} [13]). This value is a measure of the activation energy of the quaternary salt and one (together with the magnitude of $-q_{CH_2}$) of the principal criteria in the evaluation of the reactivities of methylene bases formed from the quaternary salts of such heterocycles. The lower the ΔE_{π_2} value, the more readily the quaternary salt forms a methylene compound. It is apparent from the calculated data (Table 1) that these indexes of the reactivities of quaternary salts of the examined heterocycles and their methylene bases (IX-XI and XVIII-XX) are also in good agreement with one another.

The results of the quantum-chemical study of the reactivities of the methyl groups of the examined compounds are in good agreement with the available experimental data on the lability of the hydrogen atoms in them obtained by a study of the kinetics of deuterium exchange [14] and the condensation of quaternary salts of such heterocycles with p-dimethylaminobenzaldehyde [15]. In particular, in dealing with problems in the synthesis of polymethine dyes with residues of the investigated bases, one should note that the quaternary salts of 2-methylbenzothiazoles and 2-methylthienobenzothiazoles condense quite readily with esters of higher ortho acids, whereas the salts of 2-methylthieno- and benzothieno-thiazoles do not undergo such reactions under any conditions. However, other dyes are formed from them in considerably lower yields than from the salts of 2-methylbenzothiazole. A dimethylidynemerocyanine was obtained in less than 2% yield from the quaternary salt of 2-methylbenzothieno[2,3-d]imidazole. Other dyes with residues of this base are not formed under the presently known conditions for carrying out cyanine condensations.

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