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ROLE OF THE 3d ORBITALS OF SULFUR IN THE THIAPYRYLIUM CATION

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The electronic structure of the thiapyrylium cation with allowance for and neglect of the 3d orbitals of sulfur was investigated by the self-consistent field MO LCAO method within the CNDO/2 (complete neglect of differential overlap) approximation. Inclusion of the 3d AO of sulfur in the basis leads to slight redistribution of the electron density to favor equalization of the charges on the carbon atoms. A qualitative correlation of the calculated populations of the atoms with the chemical shifts of the PMR spectrum of the thiapyrylium cation was obtained.

It was recently observed [1] that the PMR spectrum of the thiapyrylium cation (I) differs substantially from the spectrum of its analogs, pyrylium (II) and ethylpyridinium (III) cations (Table 1). The superimposition of the signals of the γ and β protons of I is explained by equality of the charges on the γ- and β-carbon atoms. In the opinion of Yoneda and co-workers, the reason for this peculiar electronic structure of the thiapyrylium cation is strong interaction of the 2p orbitals of the carbon atoms with the vacant 3d orbitals of sulfur. A conclusion regarding the substantial role of the 3d AO of sulfur in the thiapyrylium cation was drawn on the basis of a calculation of its electronic structure by the extended Huckel method (EHM).

It is known that the EHM, without self-consistency with respect to the charges and configurations, usually poorly conveys the charge distribution in heteroatomic ionic molecules [2]. A comparison of the charge distribution in I and II, obtained by the EHM, confirms this fact. In the thiapyrylium cation the calculated negative charge on the heteroatom and the contribution of carbonium valence structures to resonance are of a high order of magnitude (Table 2), despite the fact that the sulfur atom has a lower electronegativity than oxygen.

The EHM displays disadvantages especially markedly in the study of the problem of the 3d AO of elements of the third period. The absence of reliable methods for evaluation of the parameters for the outer vacant 3d orbitals usually leads to a considerable overestimation of their role in the formation of chemical bonds [4]. Ac-

TABLE 1. Chemical Shifts (δ) of the PMR Spectra of Thiapyrylium (I), Pyrylium (II), and N-Ethylpyridinium (III) Cations in Trifluoroacetic at 60 MHz

	I	II	III
α-H	10,20	9,70	8,81
β-H	9,11	8,53	8,22
γ-H	9,11	9,36	8,60

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TABLE 2. Charge Distribution in the Thiapyrylium Cation (X = S) with Allowance for (spd basis) and Neglect of (sp basis) the 3d Orbitals of Sulfur and in the Pyrylium Cation (X = O) Obtained by the CNDO/2 and EHM Methods

Atom	CNDO/2			EHM		
	X=S *(sp)*	X=S *(spd)*	X=O[3]	X=S *(sp)*[1]	X=S *(spd)*[1]	X=O[2]
X	0,27	0,27	−0,06	−1,07	−2,00	−0,69
α-C	0,11	0,02	0,25	0,88	0,93	0,60
β-C	−0,01	0,08	−0,03	−0,04	0,26	−0,14
γ-C	0,15	0,09	0,18	0,21	0,33	0,13

cording to [1], the heteroatom in the thiapyrylium cation acquires more negative charge (Table 2), as a consequence of which the acceptor capacity of its vacant 3d AO falls. Nevertheless, the population of the 3d orbitals of sulfur in I reaches 1e, according to the estimate of the authors.

For these reasons, the reliability of the results obtained in [1] is doubtful. In order to make a more precise determination of the role of sulfur in the formation of thiapyrylium compounds, we calculated cation I by the CNDO/2 (complete neglect of differential overlap) method [5-7], which gives an accurate picture of the electron density distribution in the molecules [8]. The method gives a somewhat overstated population of the outer vacant d orbitals [4], and this makes it possible to obtain the upper estimate of the degree of participation of the 3d AO of sulfur in bonding.

The geometric parameters of the thiapyrylium cation that we adopted (R_{CS} = 1.70 Å, R_{CC} = 1.40 Å [1], and < CCC = 123°) under the assumption of a planar structure insure an acceptable < CSS value and an acceptable valence angle of the sulfur atom in six-membered rings [9-13].

In contrast to the EHM and in complete agreement with the results of ab initio calculation [14], the CNDO/2 method leads to the conclusion that expansion of the basis due to the vacant 3d AO of sulfur does not lead to significant redistribution of the electron density in the thiapyrylium cation (Table 2). The charge on sulfur is retained, despite the rather large population of the 3d orbitals (0.56 e). It should be noted that their real population is apparently lower. Only 36% of this density goes into the $3d_\pi$ orbitals, and the role of $p_\pi-d_\pi$ conjugation in the I cation therefore cannot be large. The effect of the 3d AO of sulfur reduces to a certain equalization of the charges on the carbon atoms (principally due to a shift of the electron density from the β- to the α-carbon atoms).

The charge distribution in the thiapyrylium cation (spd basis) is characterized by close (in magnitude) electron densities on the carbon atoms and a positive charge on sulfur on the order of 0.27 e. This result is in very good agreement with the results of calculation by a nonempirical method [14]. We also note that, in conformity with the low electronegativity of the sulfur atom in the thiapyrylium cation, the electron density on the heteroatom is considerably lower, and the electron density on the α- and γ-carbon atoms is considerably higher than in its oxygen analog II (Table 2).

The equality of the charges on the β-C and γ-C atoms in I explains the superimposition of the signals of the β and γ protons in the PMR spectrum (Table 1), and the increase in the electron density in the order γ-C (II) < γ-C (I) ≈ β-C (I) < β-C (II) is in agreement with the decrease in the chemical shifts (δ) in the order γ-H (II) > γ-H (I) ≈ β-H (I) > β-H (II). The appearance of the signal of the α protons at I at weaker field (δ 10.20) than the absorption of the α protons of II (δ 9.70) is evidently due to the magnetic anisotropy of the sulfur atom [1].

Thus a peculiarity of the structure of I is the uniform character of the electron density distribution over the carbon atoms; this is reflected in the PMR spectrum. Allowance for the 3d orbitals appreciably improves the picture of the charge distribution in the thiapyrylium cation. However, the conclusion that the peculiarity of its electronic structure is due to $p_\pi-d_\pi$ conjugation is not confirmed [1].

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INDOLE DERIVATIVES

XLV.* CYCLIZATION OF 2-(β-AMINOISOBUTYL)INDOLE WITH GLUTARIC ANHYDRIDE AND OPIANIC ACID

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New γ-carboline derivatives were synthesized on the basis of the reaction of 2-(β-aminoisobutyl)-indole with glutaric anhydride and opianic acid.

It is known [2] that indoles condensed with quinolizine or indolizine rings, derivatives of which have pronounced pharmacological activity, can be obtained by reaction of tryptamines with 1,4- and 1,5-dicarbonyl compounds. In connection with the fact that we have previously [3] developed the synthesis of compounds of the isotryptamine series, in particular, 2-(β-aminoisobutyl)indole (I), we undertook a study of the reactions of I with glutaric anhydride (II) and opianic acid (III). The reaction of I with II proceeds smoothly to give glutaric acid polyamide (IV), which was converted to ester (V) by the action of diazomethane. Under the influence of phosphorus oxychloride, ester V undergoes cyclization to a substituted 1,2-dihydro-γ-carboline, and, depending on the conditions used to work up the reaction mixture, the ester grouping is retained or undergoes partial hydrolysis to give, respectively, acids VIa and VIb. Ester VIb was converted to a substituted 1,2,3,4-tetrahydro-γ-carboline (VII) by hydrogenation over platinum. (See scheme on following page.)

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*See [1] for communication XLIV.

TABLE 1. Data on IV-VIII

Compound	mp, °C*	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	Cl	N	C	H	Cl	N	
IV	159,5—161	$C_{17}H_{22}N_2O_3$	67,3	7,3		9,2	67,5	7,3		9,3	60
V	82—83	$C_{18}H_{24}N_2O_3$	68,5	7,7		9,2	68,3	7,6		8,8	93
VIa	251—252	$C_{17}H_{20}N_2O_2$	71,9	7,3		10,1	71,8	7,1		9,8	50
VIb	143,5—145	$C_{18}H_{22}N_2O_2 \cdot HCl$	64,3	6,8	10,4	8,4	64,5	6,9	10,6	8,4	85
VII	191—192	$C_{18}H_{24}N_2O_2 \cdot HCl$	64,1	7,5	10,4	8,4	64,2	7,5	10,5	8,3	75
VIIIa	216—217	$C_{23}H_{26}N_2O_4 \cdot HCl$	63,7	6,2	8,0	6,7	64,1	6,3	8,2	6,5	83
VIIIb	204—205	$C_{24}H_{28}N_2O_4 \cdot HCl$	64,5	6,5	8,0	6,7	64,8	6,5	7,9	6,3	55

*Compounds V, VIIIa, and VIIIb were recrystallized from alcohol, V was recrystallized from benzene–petroleum ether, VIa and VII were recrystallized from isopropyl alcohol–ether, and VIb was recrystallized from methanol.

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