HMO STUDY OF MONOHYDROXYPYRIDINES AND THEIR BENZODERIVATIVES

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Fifteen monohydroxyderivatives of pyridine, quinoline, isoquinoline, acridine, and phenanthridine were studied by simple HMO method. Interrelations between π-electron densities (chemical reactivity indices) and tautomerism or experimental reactivity of individual compounds are discussed. Some correlations of theoretical quantities with spectral data were established.

Within the framework of the study of the applicability of HMO theory in the field of chemistry of heterocyclic compounds we were interested in some hydroxyderivatives of pyridine and benzoderivative thereof. These compounds, in which possibility of keto-enol tautomerism must be considered (*e.g.* hydroxypyridine–pyridone), can participate in chemical reactions in two molecular forms. It was thus desirable to ascertain whether and how correctly HMO method interprets hitherto experimental data on the studied type of compounds on condition that HMO models of both tautomeric forms are considered.

Mason showed[1] that on the basis of perturbation treatment and certain approximations, HMO π-electron densities on the nitrogen can be applied with success to estimation of tautomerism in compounds *I*–*XII*. With the same purpose also differences in vertical delocalization energies[2] and π-bonding energies[3] of the models of corresponding tautomers were suggested. The simple HMO method proved to be fruitful also in the interpretation of reactivity of 1-methyl-1-pyridone[4] and methylderivatives[4] thereof, and of 3-hydroxypyridine (*II*) (ref.[5]). In contrast, Evleth[6] and Zanker and coworkers[7] were able to interpret satisfactorily the electronic spectra of isomeric 1-methylpyridones and hydroxyacridines only with the aid of the method of limited configurational interaction (LCI).

In the present work we wish to report the data obtained in the HMO calculation of both tautomeric forms of compounds I–XV, represented by formula of the prevailing tautomer.*

* Except for compound *X*, the prevailing tautomeric form of which is not known. The enol- and ketoforms are denoted by letters *e* and *k*, resp., *e.g. Ie*, *Ik*.

CALCULATIONS

Coulomb and resonance integrals in the HMO method were defined in the usual way

$$\alpha_X = \alpha_C + h_X\beta_{CC} \quad \text{and} \quad \beta_{CX} = k_{CX}\beta_{CC},$$

where h_X and k_{CX} are the empirical parameters and the other quantities were conventionally taken as $\alpha_C = 0$ and $\beta_{CC} = 1$. The following values of parameters, recommended by Streitwieser[8] were employed: $h_{NH} = 1{\cdot}5$, $h_O = 1{\cdot}0$, $k_{CN(H)} = 0{\cdot}8$ and $k_{CO} = 1{\cdot}0$ (for ketoforms), and $h_N = 0{\cdot}5$, $h_{OH} = 2{\cdot}0$, $k_{CN} = 1{\cdot}0$ and $k_{CO(H)} = 0{\cdot}8$ (for enolforms). All the calculations were carried out with the aid of standard HMO programs (designed by Drs V. Kvasnička and J. Pancíř) on NE 803B and E503 digital computers in the Computer Center of this Institute. Basic energetic data on compounds *I*—*XV* are summarized in Table I: *W* stands for total π-electron

TABLE I

Energy Data for HMO Models of Compounds *I*—*XV*

All the data are given in β-units.

Compound	Enolform					Ketoform				
	W	k_2	k_1	k_{-1}	k_{-2}	*W*	k_2	k_1	k_{-1}	k_{-2}
I	12·767	1·155	0·860	−0·862	−1·060	12·102	1·436	0·645	−0·553	−1·139
II	12·746	1·131	0·841	−0·850	−1·055	11·904	1·238	0·518	−0·436	−1·113
III	12·761	1·000	0·964	−0·912	−1·000	12·058	1·000	0·964	−0·614	−1·000
IV	18·465	0·909	0·686	−0·555	−1·034	17·916	0·849	0·717	−0·430	−1·051
V	18·434	0·913	0·655	−0·540	−1·034	17·659	0·891	0·497	−0·286	−1·061
VI	18·483	1·000	0·640	−0·583	−1·000	17·879	1·000	0·714	−0·477	−1·000
VII	18·446	1·000	0·606	−0·564	−1·000	17·741	1·000	0·482	−0·341	−1·000
VIII	18·441	0·912	0·664	−0·544	−1·034	17·728	0·885	0·558	−0·328	−1·056
IX	18·467	1·072	0·585	−0·632	−0·920	17·883	1·000	0·570	−0·578	−0·782
X	18·445	1·023	0·590	−0·580	−0·974	17·734	1·083	0·440	−0·372	−0·941
XI	18·436	1·076	0·671	−0·614	−0·922	17·618	1·000	0·397	−0·381	−0·824
XII	18·437	0·944	0·618	−0·597	−0·940	17·668	0·758	0·556	−0·429	−0·777
XIII	18·443	1·074	0·568	−0·619	−0·921	17·690	1·000	0·449	−0·436	−0·815
XIV	24·145	1·000	0·462	−0·393	−1·000	23·706	1·000	0·671	−0·390	−1·000
XV	24·244	0·777	0·628	−0·574	−0·770	23·754	0·856	0·672	−0·505	−0·779

energies, k_{-1} and k_{-2} are the energies of the two lowest antibonding MO's, k_1 and k_2 are the energies of the two highest bonding MO's. On calculating delocalization energies for Kekule structures we used the following values of energies: $W_{NH} = 3{\cdot}000\,\beta$, $W_{C=O} = 3{\cdot}236\,\beta$, $W_{OH} = 4{\cdot}000\,\beta$, and $W_{C=N} = 2{\cdot}562\,\beta$.

RESULTS AND DISCUSSION

Tautomerism

In Fig. 1 are represented molecular diagrams of both tautomeric forms of isomeric monohydroxypyridines *I*–*III*. It is evident that both forms have characteristic π-electron distribution. Whereas π-bond orders in the heterocyclic ring of enolforms *Ie*–*IIIe* indicate an "aromatic" character of all the bonds, π-bonds in ketoforms *Ik*–*IIIk* appears to be more localized in the sense of classic formulae *I* and *II*. The latter finding is in accordance with the data obtained in the HMO calculation of 1-methyl-2-pyridones[4], and, with regard to the wellknown fact that the simple HMO method strongly overestimates conjugation[8,9], it can be taken as an argument for the concept of "nonaromatic" character of bonds in pyridones.

There is a number of experimental data indicating that compounds *I*, *III*, *IV*, *VI*, *IX*, *XIV* and *XV* exist predominantly as ketones, while compounds *II*, *V*, *VII*, *VIII*, *XI* and *XIII* as enols (*cf.*[1,10–20]). This seems to indicate that the possibility of formation of the ring with aromatic character in the compounds studied is not the determining factor of the stability of individual tautomers. We have found that by simple comparison of absolute values of HMO energies (*W*, *DE* or *BE*) for individual couples of tautomers the prevailing form cannot be predicted. Gold did recommend[3] HMO values of π-bond energies *BE* as suitable quantities for the estimation of stability of both forms of compound *I*. However, we have not been able to repeat his calculation, since the author did not report parametrization of his HMO models. On using our values of parameters h_X and k_{CX} we have obtained for compound *I* $BE_e > BE_k$ (indices *e* and *k* denote the enol- and ketoform, resp.), in contrast to the reported[3] sequence $BE_k > BE_e$ by using both Gold's definition[3] of *BE* and the definition taking into account the number of π-electrons, by which the individual atomic orbitals contribute to the conjugation[21] ($BE_e = 10{\cdot}267$ and $8{\cdot}267\beta$, resp., and $BE_k = 9{\cdot}602$ and $8{\cdot}102\beta$, resp.) The absolute values of HMO energies undoubtly depend on the parametrization chosen. As for tautomerism in our case a thermodynamically controlled equilibrium between two molecules can be expected, a more correct, alternative approach should consist in estimation of differences in energies $\Delta W = W_e - W_k$, where W_k and W_e are the calculated π-electron energies of tautomers compared. The use of analogical differences ΔBE or ΔDE in the case of the series of compounds studied here is meaningless since it can be easily shown that

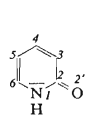
$$\Delta W = \Delta BE + C = \Delta DE + C' ,$$

where *C* and *C'* are the constants defined as follows

$$C = h_N - h_O + 2(h_{OH} - h_{NH}) = 0{\cdot}500\beta ,$$

$$C' = W_{C=N} + W_{OH} - W_{C=O} - W_{NH} = 0{\cdot}326\beta .$$

In Fig. 2 are plotted the logarithms of tautomeric equilibrium constants ($K_t = c_{keto}/c_{enol}$) determined by Mason[1] and Albert and Phillips[11] against the energy difference ΔW. It is evident that there exists an approximatelly linear correlation between these two quantities. This indicates that π-electron system in compounds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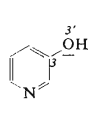
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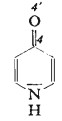
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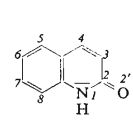
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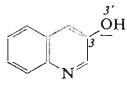
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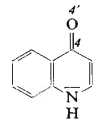
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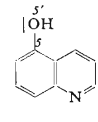
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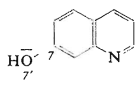
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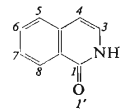
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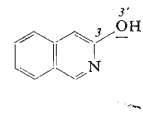
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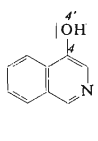
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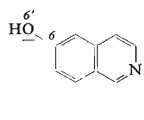
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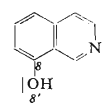
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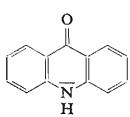
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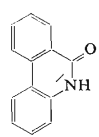
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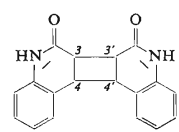
XVI

I–IX, and *XI–XV* significantly affects tautomeric equilibrium, however, together with other factor which cannot be rendered by the simple HMO calculation. The negative value of the slope in Fig. 2 may be explained on the basis of the assumed shift enolform → ketoform, which is the more difficult, the smaller is the change in π-electron energy.

Chemical Reactivity

There exists a relatively large number of data in the literature on the reactivity of studied compounds in their reactions with some electrophilic agents. In Table II is presented comparison of prediction of relative reactivity of individual positions in compounds *I–IV*, *VI*, *VII*, *IX*, *XIV*, and *XV* based on calculated π-electron densities q, electrophilic superdelocalizabilities S_e, and Wheland electrophilic localization energies L_e with corresponding experimental data. It is evident that theoretical prediction of the most reactive position in most cases does not depend significantly on the kind of the index used. Also differences between prediction based on the keto- and that based on the enolforms are not so significant as to allow, by compari-

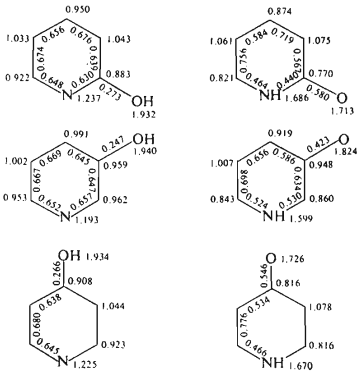

FIG. 1

HMO Molecular Diagrams of Both Tautomeric Forms of Monohydroxypyridines
For parametrization see Calculations.

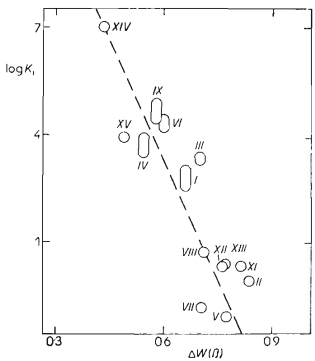

FIG. 2

Plot of Logarithms of Tautomeric Equilibrium Constants K_t for Compounds *I–IX*, *XI–XIII* (ref.[1,11]) against Differences of π-Electron Energies ΔW, for HMO Models of Enol- and Ketoforms

TABLE II

Reactivity of Individual Positions in Compounds *I—IV, VI, VII, IX, XIV* and *XV* towards Electrophilic Agents[a]

Compounds	Prediction based on index[b]		Experiment	Reaction
	q	$S_e(L_e)$		
Ie	2′ > 3 > 5	2′ > 3 > 5	2′; 2′ a 1	alkylation[24], acylation[25]
		(2′ > 1 > 3 > 5)		phenylation[27], amination[28]
				addition over activated C=C bond[26,29,30]
Ik	2′ > 1 > 3	2′ > 3 > 5	3 > 5	nitration[31], chlorination[32]
		(2′ > 1 > 3 > 5)	3 a 5	bromination[33], iodination[32,34]
IIe	3′ > 1 > 5	3′ > 2 > 5	3′	acylation[25]
		(3′ > 1 > 2 > 4)	2	iodination[44], sulphonation[35]
IIk	3′ > 1 > 5	3′ > 2 > 6		hydroformylation[36], addition
		(3′ > 1 > 2 > 6)		over activated C=C bond[37]
			2 > 6	nitration[38]
IIIe	4′ > 1 > 3	4′ > 3 > 1	4′	addition over activated C=C bond[26]
		(4′ > 1 > 3)	3 a 5	nitration[39,40], bromination[41]
IIIk	4′ > 1 > 3	4′ > 3 > 1		iodination[34]
		(4′ > 1 > 3)	1	alkylation[41]
IVe	1 > 2′ > 3 > 6	1 > 8 > 2′ > 5	1 > 2′; 2′	amination[28], alkylation[42]
		(2′ > 1 > 8 > 5)	6; 6 > 3	nitration[43], bromination[44],
IVk	1 > 2′ > 3 > 8	2′ > 1 > 3 > 8		chlorination[44]
		(1 > 2′ > 3 > 8)		
VIe	4′ > 1 > 3	1 > 3 > 4′	4′	alkylation[45]
VIk	1 > 4′ > 3	4′ > 1 > 3	1	alkylation[46]
VIIe	5′ > 1 > 6 > 8	8 > 5′ > 6 > 1	8	coupling[47]
		(5′ > 1 > 8 > 6)	8 > 6	bromination[48]
VIIk	5′ > 1 > **6** > **8**	**5′ > 6 > 8** > 1		
		(5′ > 1 > 6 > 8)		
IXe	1′ > 2 > 4	4 > 1′ > 2	1′	alkylation[49]
IXk	2 > 1′ > 4	1′ > 4 > 2	2	alkylation[49]
XIe	4′ > 2 > 8	4′ > 3 > 10	3	nitration[50], addition over
XIk	4′ > 2 > 8	4′ > 3 > 1		activated C=C bond[51]
XIVe	9′ > 10 > 11 > 4	10 > 4 > 9′ > 2	2 > 4; 2	nitration[52], sulphonation[53,54]
XIVk	10 > 9′ > 11 > 4	9′ > 10 > 4 > 2		chlorination[55]
			2 a 3	bromination[56]
XVe	10′ > 9 > 8	9 > 8 > 10′	9	alkylation[57]
XVk	9 > 10′ > 8	10′ > 9 > 8	5	nitration[58]

[a] The reactions in which the compound followed behaves as nucleophile (*e.g.* additions over activated multiple bonds[26,29,30,37,51]) are also included. [b] Meaning of symbols: q π-electron density, S_e electrophilic superdelocalizability, L_e Wheland electrophilic atom localization energy. Numerical values of the indices of chemical reactivity will be sent on request.

TABLE III

Reactivity of Individual Positions in Compounds *I*, *II*, *IV*, *VI*, *VII*, *IX*, *XIV* and *XV* towards Nucleophilic Agents

Compound	Prediction based on index[a]			Experiment	Agent	Ref.
	q	$S_n(L_n)$				
Ie	2 > 6 > 4	6 > 4 > 2	(6 > 4 > 2)	2	PCl_5 + $POCl_3$	59
Ik	2 > 6 > 4	6 > 4 > 2	(6 > 4 > 2)			
IIe	6 > 3 > 2	2 > 4 > 6	(2 > 4 > 6)	2	NaOH(melting)	60
IIk	6 > 2 > 4	2 > 6 > 4	(2 > 6 > 4)	2, 4	$NaNH_2$	35
IVe	2 > 4 > 7	4 > 2 > 5	(4 > 5 > 8)	2	PBr_3, PCl_5 + $POCl_3$	62,61
IVk	2 > 4 > 7	4 > 2 > 5	(4 > 5 > 2)	2	P_2S_5	63
VIe	4 > 2 > 6	4 > 2 > 6		4	PCl_5 + $POCl_3$	64
VIk	4 > 2 > 7	2 > 4 > 5		4	PhCOCl	65
VIIe	2 > 4 > 5	4 > 2 > 5	(4 > 2 > 8)	2	KOH (melting)	66
VIIk	2 > 4 > 5	2 > 4 > 7	(2 > 4 > 7)			
IXe	1 > 3 > 8	1 > 8 > 5		1	PCl_5 + $POCl_3$	67
IXk	1 > 3 > 8	1 > 3 > 8		1	PBr_3	68
XIVe	9 > 1 > 3	9 > 1 > 3		9	PCl_5 + $POCl_3$	69
XIVk	9 > 1 > 3	9 > 1 > 3		9	P_2S_5	70
XVe	10 > 1 > 3	10 > 1 > 3		10	PCl_5 + $POCl_3$	57
XVk	10 > 1 > 3	10 > 1 > 5				

[a] Meaning of symbols: *q* π-electron density, S_n nucleophilic superdelocalizability, L_n Wheland nucleophilic atom localization energy.

TABLE IV

Comparison of Relative Values of Squares of Expansion Coefficients LFMO and of Reducibility of Individual Positions in Compounds *IV*, *V*, *VII* and *XIV*

Compound	Order of c_i^2 in positions *i*[a]	Experiment[a]	Reduction
IVe	4 > (5 > 1 > 8)	4 (3)	electrochemical[71]
IVk	4 > (2 > 5 > 3)		
Ve	4 > (1 > 2 > 10)	4 (3, 2, 1)	electrochemical[71]
Vk	2 > (4 > 1 > 10)		
VIIe	4 > (1 > 5 > 2)	4 (3, 2, 1)	by zinc[72], electrolytical[71]
VIIk	4 > (2 > 1 > 7)		
XIVe	9 > (10 > 1 > 3, 4)	9 (9′)	by alkali metals[73–75]
XIVk	9 > (9′> 1 > 3)		

[a] The first number denotes the position with the highest values of c_i^2 (LFMO) in which reduction apparently begins to proceed.

son with experimental data, a reliable prediction of the more reactive tautomeric form. With monocyclic compounds *I—III* the higher reactivity on the heteroatoms for reactions with carbon reagents (*e.g.* alkyl and acyl ones) is correctly predicted. By analogy with the products formed by reactions of compounds *II*, *III* and *VI* with diazoalkanes $R—\overset{\delta-}{C}H=N=\overset{\delta+}{N}$ [22,23] one can assume that the above alkylation agents attack the heteroatoms of the substrate at first by electron-deficient nitrogen atom of the molecule, this being followed by formation of the C—N or C—O bonds. Nitration and chlorination likely proceed *via* protonization of the heteroatoms, and thus the products which are isolated are those formed by the attack on the other position (in the order of their reactivity, *i.e.* positions 3 and 5 in compounds *I* and *III*, and position 2 and 6 in compound *II*). With polycyclic compounds the reactivity is correctly predicted only when the reactions take place on the rings bearing the heteroatom or substituent (*i.e.* all electrophilic reactions of compounds *VI*, *VII*, *IX*, *XI* and alkylation of compound *XV*). In contrast, the HMO prediction for reactions of unsubstituted condensed benzene ring is quite unreliable (see reactions of compound *XIV*, nitrations of compounds *IV* and *XV*, and halogenations of compound *IV*).

Table III presents comparison of the prediction of the relative reactivity of individual positions towards nucleophilic agents based on π-electron densities q, superdelocalizabilities S_n, and localization energies L_n with experimental data. It seems that for reactions with weak nucleophiles such as PCl_5, PCl_3 and P_2S_5 π-electron density on the carbon atom bonded to the most electronegative atom(oxygen) becomes the decisive factor; in all cases the index q correctly predicts the reaction. The reactions of compound *II* with strong nucleophiles such as NaOH and $NaNH_2$ are better interpreted by indices L_n and S_n. This case is however more complicated since also anions formed by reaction of the starting compound with the alkali can participate in the reaction. Thus here some HMO models of the forms considered by us might be considered as relevant also for these anions.

Compounds *IV*, *V*, *VII* abd *XIV* can be selectively reduced electrochemically or by the action of metals[71–75]. A promotion of one or two electrons to LFMO of the substrate can be regarded as the first stage of these reactions. In the positions with the highest probability of the occurence of the electrons in the above MO's one can expect an attack by protons to form corresponding CH, OH or NH bonds. In Table IV are compared relative values of squares of expansion coefficients LFMO with experimentally found course of above reductions. The first number denotes the most reactive position, in the region of which electrons from the reducing agent are predominantly localized. It is evident that the agreement obtained is quite good.

We have further attempted to interpret interesting photodimerization of compound *IV*, which yields 3,3'-4,4'-dimer *XVI* [76]. With this purpose we compared the values of free valences F for ground electron states of both tautomers *IVe* and *IVk*

with respective values of F^* for their single-electron excited states (the $N \rightarrow V_1$ transition, Table V). The values of F^* for prevailing ketoform *IVk* are greatest in positions 3 and 4, which correctly predicts the course of the above reaction. Similarly as in the case of 1-methyl-2-pyridone[4] also here very simplified HMO treatment proved to be suitable for interpretation of photochemical reaction.

Physical Properties

We made an attempt to correlate the wavenumber of the longest-wavelength absorption band maxima, $\tilde{\nu}_{max}$, in the ultraviolet spectra of compounds *I–IX*, and *XIV*[77–79] with theoretical energies $E(N \rightarrow V_1)$, calculated for models of both enol- and ketoforms of these compounds. In the case of the enolforms (Fig. 3) there is a distinct tendency to correlation between the two quantities followed. Correlation field is however rather dissected according to the size of the molecules. In the second case (ketoforms, Fig. 4) the data are grouped into the two independent correlations; the one belongs to compounds *I*, *III*, *IV*, *VI*, *IX*, *XIV* (prevailing ketoform;

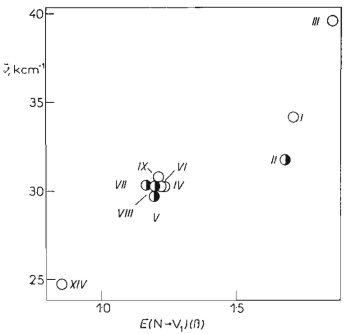

FIG. 3

Dependence of $\tilde{\nu}_{max}$ of the Longest Wavelength Absorption Band in Electronic Spectra of Compounds *I–IX* and *XIV*[77–79] on the Energy $E(N \rightarrow V_1)$ of the $N \rightarrow V_1$ Transition Calculated by HMO Method for Models of Enolforms

○ Compounds exist as ketones; ◑ compounds exist as enols.

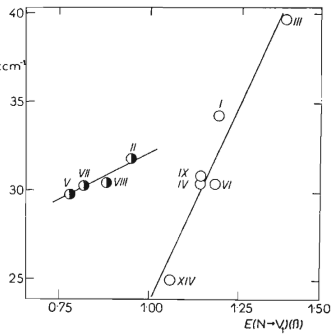

FIG. 4

Dependence of $\tilde{\nu}_{max}$ of the Longest Wavelenght Absorption Band in Electronic Spectra of Compounds *I–IX*, and *XIV* (ref.[77–79]) on the Energy $E(N \rightarrow V_1)$ of the $N \rightarrow V_1$ Transition Calculated by HMO Method for Models of Ketoforms

○ The ketoform is prevailing; ◑ the enolform is prevailing.

TABLE V

Free Valences Calculated for Ground and Excited ($N \rightarrow V_1$) States for Both Tautomers of Compound *IV*

Position	Ketoform (*IVk*)		Enolform (*IVe*)	
	F	*F**	*F*	*F**
3	0·442	0·651	0·421	0·493
4	0·476	0·629	0·453	0·659
5	0·452	0·509	0·452	0·674
6	0·399	0·449	0·404	0·124
7	0·414	0·520	0·405	0·480
8	0·422	0·440	0·450	0·681

TABLE VI

Comparison of Spin-Spin Coupling Constants (J_{HH}) in the PMR Spectrum of 9-Acridone (*XIV*) with HMO π-Bond Orders

Bond $i-j$	J_{HH} (c/s) (ref.[81])	$p_{i,j}$
1—2	8·3	0·696
1—3	1·4	0·041
1—4	0·4	—0·336
1—10	0·4[a]	0·033
2—3	7·0	0·636
2—4	1·0	—0·029
3—4	8·6	0·685

[a] In contrast to other cases, one hydrogen atom is bonded to the heteroatom.

$\tilde{\nu}_{max}(kcm^{-1}) = 43{\cdot}1\ E(N \rightarrow V_1)\ \beta - 19{\cdot}6)$, the other belongs to compounds *II*, *V*, *VII*, *VIII* (prevailing enolform; $\tilde{\nu}_{max}\ (kcm^{-1}), = 10{\cdot}1\ E(N \rightarrow V_1)\ \beta + 21{\cdot}8)$. It cannot be thus unambiguously ascertain which of the HMO models is more suitable for interpretation of the long-wavelength transitions.

There is a certain tendency, however, not statistically significant correlation, of π-electron densities in the HMO models of compounds *I*—*III* to increase with increasing values of NMR proton chemical shifts[80]. Even the use of π-electron densities calculated by Evleth[6] by SCF method in place of our HMO data has not resulted

in significant improvement. Similar interrelation between theoretical and experimental NMR data is observed also when comparing HMO π-bond orders (p) with spin-spin coupling constants (J_{HH}), which is shown in the case of 9-acridone (XIV)[81] in Table VI.

CONCLUSION

It can be stated that the simple HMO method, despite of its strongly approximative character, satisfactorily interprets hitherto experimental data on the chemical properties of studied compounds. This quantum-chemical approach, based on estimation of values of chemical reactivity indices fails to give a true picture of the reactivity of aromatic ring of benzoderivatives (*e.g.* IV and XV), in the HMO models of which Coulomb or exchange integrals are not changed on these rings as the result of the introduction of a substituent or an heteroatom. The results show that in most of the reactions studied tautomerism does not affect significantly the order of reactivity of the individual positions of the π-electron system.

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Note added in proof: When this paper was prepared for print, the publication became available to us, devoted also to HMO studies of the substances *Ie*, *Ik*, *IIe*, *IIk*, as well as of their protonated and ionized forms (V. P. Zvolinskij, M. E. Perel'son, I. N. Šejnker: Teoret. Exp. Chim. *5*, 160 (1969). Although a slightly different parametrization of the HMO models was employed, many reactivity indices, reported by the mentioned authors lead to conclusions on the reactivity identical with our results. The SCF-MO calculations of *Ie*, *Ik*, *IIe*, *IIk*, *IIIe*, and *IIIk* (L. Paoloni, M. L. Tosato, M. Cignitti: Theoret. Chim. Acta *14*, 221 (1969)) gave slighty different π-electron distributions only for *IIe* and *IIIe*.

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