SEMIEMPIRICAL SCF MO STUDY
OF METHYLPYRIDINES

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π-Electron structure of monomethylpyridines $II-IV$ and their protonated forms $II.H^+-IV.H^+$ was examined with the aid of Pople version of the SCF-MO-LCAO method. The calculated characteristics of π-electron distribution were confronted with the corresponding HMO quantities, chemical reactivity and PMR data. The electronic absorption spectra of the studied compounds were interpreted with the aid of LCI method.

Recent HMO studies of methylpyridines demonstrated that surprisingly good interpretation of various experimental data, in particular chemical reactivity, can be achieved by using this very simplified approach[1-7]. It was thus interesting to ascertain how this interpretation would be changed when the more perfect type of self-consistent MO's would be used in place of Hückel ones.

In the present work we wish to report the results of SCF calculations of monomethylpyridines $II-IV$ and corresponding protonated forms $II.H^+-IV.H^+$. The results obtained were confronted with the analogous data for pyridine (I) and its protonated form $I.H^+$.
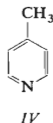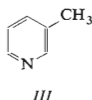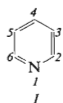
CALCULATIONS

The SCF models of the studied compounds were calculated with the use of the Pople-Pariser-Parr version[8-10]. The effect of methyl group on π-electron system was estimated by means of hyperconjugation model[11]. (The heteroatom model was not applied here since preliminary SCF

calculations applied showed that the use of parametrization similar to that employed in the work[12] leads to the values of theoretical electronic transitions in compounds $II-IV$ which differ from those experimentally found by 1·2 to 6·0 eV). Hückel molecular orbitals with corrected resonance integrals were taken as the starting approximation. Hyperconjugation model of methyl group (see ref.[13]) was used in obtaining HMO data needed for the comparison with SCF calculations. The parametrization used is given in Table I. The following geometry of compounds $I-IV$ was considered in the SCF calculations: the idea heterocyclic ring with the C—C and C—N bond lengths 1·4 Å and the bond angles 120°, the C—CH$_3$ bond length 1·52 Å and the C—H bond length 1·1 Å. The models of molecules were located in the plane xy always in such a way

TABLE I

Parameters for SCF and HMO Calculations

	SCF				HMO		
Atom	I eV	A eV	Lit.	$h_X{}^a$	Bond	k_{CX}	Lit.
C (sp^2)	11·16	0·03	14	0	C—N	1·0	13
N (sp^2)	14·12	1·78	14	0·5	C—N^{+b}	1·0	13
N$^+$ (sp)^2	13·65	2·53	14	2·0	C—CH$_3$	0·8^c	13
C(H$_3$)	11·42	0·58	15	−0·1	C—(H$_3$)	3·0^c	13
H$_3$(C)	9·50	0	15	−0·5			13

^{a} For null iteration in all SCF calculations $h_X = 0$. ^{b} In protonated forms. ^{c} For SCF calculation $k_{C-CH_3} = 0.51$ and $k_{C-(H_3)} = 1.25$ (ref.[15]).
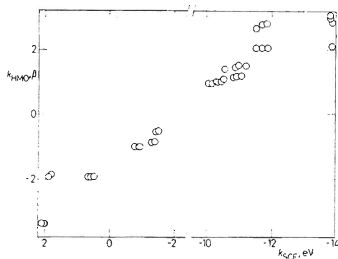

Fig. 1

Plot of Self-Consistent Molecular Orbital Energies against Hückel MO Energies for Compounds $I-IV$ and $I . H^+ - IV . H^+$

TABLE II
HMO and SCF π-Electron Energies for Compounds Studied

Method	MO	I	I . H⁺	II	II . H⁺	III	III . H⁺	IV	IV . H⁺
SCF[a]	2′	— 0·891	— 0·922	— 0·889	— 0·913	— 0·906	— 0·936	— 0·783	— 0·812
	1′	— 1·411	— 1·532	— 1·350	— 1·473	— 1·345	— 1·462	— 1·416	— 1·527
	1	—10·413	—10·447	—10·067	—10·100	—10·072	—10·102	—10·311	—10·343
	2	—11·058	—11·118	—10·904	—10·955	—10·827	—10·879	—10·494	—10·541
	W^b	80·092	79·909	105·043	104·860	105·034	104·852	105·042	104·860
HMO[c]	2′	— 1·000	— 1·000	— 1·016	— 1·016	— 1·016	— 1·016	— 1·000	— 1·000
	1′	— 0·841	— 0·507	— 0·850	— 0·530	— 0·845	— 0·509	— 0·864	— 0·538
	1	— 1·000	— 1·000	— 0·944	— 0·948	— 0·939	— 0·942	— 1·000	— 1·000
	2	— 1·167	— 1·507	— 1·161	— 1·505	— 1·146	— 1·450	— 1·084	— 1·397
	W^b	8·549	10·698	14·132	16·307	14·121	16·268	14·128	16·295

[a] All data in eV. [b] Total π-electron energies. [c] All data in β-units.

TABLE III
Free Valences in SCF and HMO Models of Compounds Studied ($N_{max} = \sqrt{3}$)

Compound	F^{SCF} in position					F^{HMO} in position				
	2	3	4	5	6	2	3	4	5	6
I	0·414	0·398	0·401	0·398	0·414	0·409	0·398	0·402	0·398	0·409
II	0·268	0·406	0·400	0·400	0·413	0·250	0·409	0·401	0·400	0·413
III	0·422	0·254	0·409	0·398	0·415	0·420	0·238	0·412	0·397	0·415
IV	0·413	0·405	0·256	0·405	0·413	0·407	0·407	0·245	0·407	0·413
I . H⁺	0·416	0·398	0·403	0·403	0·416	0·515	0·389	0·439	0·389	0·416
II . H⁺	0·269	0·406	0·402	0·399	0·416	0·354	0·403	0·434	0·389	0·417
III . H⁺	0·425	0·254	0·411	0·397	0·417	0·529	0·229	0·447	0·387	0·516
IV . H⁺	0·416	0·404	0·258	0·404	0·416	0·510	0·397	0·285	0·397	0·510

that the center of the ring corresponded to the center of coordinate system, either pseudomethyl group $-C{\equiv}H_3$ or the heterocyclic nitrogen being oriented in the positive or in the negative direction of the axis y, respectively. Theoretical quantities were converted into physical units by using $\beta = -2.388$ eV.

RESULTS AND DISCUSSION

Comparison of SCF with HMO Data

In Table II are given total π-electron energies, W^{SCF} and W^{HMO}, the energies of the two highest occupied MO's, k_1 and k_2 and of the two lowest unoccupied MO's, $k_{1'}$ and $k_{2'}$. The comparison of all the SCF orbital energies with analogical data obtained by the simple HMO method (Fig. 1) shows that there exists a significant parallelity between both quantities; only the energy difference between the bonding and the antibonding MO's is somewhat greater in the SCF approximation. In Figs 2 and 3 are compared the SCF and HMO molecular diagrams of 2-methylpyridine (*II*) and 2-methylpyridinium (*II . H*$^+$). It can be stated that the differences between both versions of MO method, shown by π-electron distributions, are for the neutral molecule of pyridine (*II*) quite insignificant (Fig.2). A more significant difference can be seen in the case of the cation *II . H*$^+$ (Fig. 3). We believe this difference can be accounted for by the fact that the value of parameter $h_N = 2.0$ used[13] for HMO models of protonated forms (see "Calculations") is too high. It seems that a more suitable value would be $h_N = 1.5$. The situation in the SCF and HMO models of compounds *I, I . H*$^+$, *III, III . H*$^+$, *IV* and *IV . H*$^+$ is quite analogical.
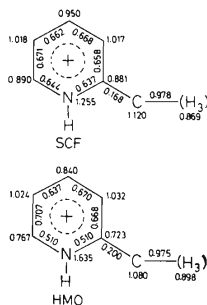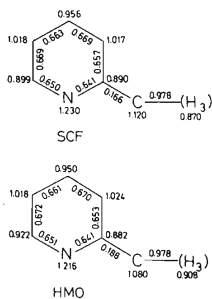

FIG. 2

Molecular Diagrams of 2-Methylpyridine (*II*)

FIG. 3

Molecular Diagrams of 2-Methylpyridinium (*II . H*$^+$)

Chemical Reactivity

The systematic confrontation of various experimental data relating to the reactivity of the heterocyclic ring in compounds $I-IV$ with different HMO indices of chemical reactivity was for compounds $II-IV$ and other methylpyridines performed in our previous studies[4,6]. A qualitative nature of most experimental data on heterolytic reactions (see references in the work[4]) prevented us from estimating the suitability of SCF and HMO indices. In contrast, substantially more extensive collection of experimental data[3,16-18] on radical substitutions of bases $I-IV$ and conjugated acids $I . H^+ - IV . H^+$ seems to be suitable for this purpose. As it was shown earlier[5], the use of hereroatom model[13] of methyl group within the framework of the simple HMO method leads to a statistically significant correlation of free valence F with logarithms of partial rate factor $\log k$ for phenylation of compounds $I-IV$[3,16,17] not however with analogical experimental data for the identical transformations studied in the work[18]. Fig. 4 demonstrates that essentially "homogeneous" correlation is preserved even in case where the hyperconjugation model of methyl group[13] is applied $\left(\log k = 28 \cdot 04 F^{HMO} - 11 \cdot 13; \ r = 0 \cdot 9559 \ \text{for 13 couples}\right)$. A similar correlation with free valence F^{SCF} is shown in Fig. 5 $\left(\log k = 22 \cdot 98 F^{SCF} - 9 \cdot 09; \ r = 0 \cdot 8957\right)$. The latter correlation is not so good as the former one, in spite of hitherto experience that the use of SCF reactivity indices in place of HMO ones results in a better agree-
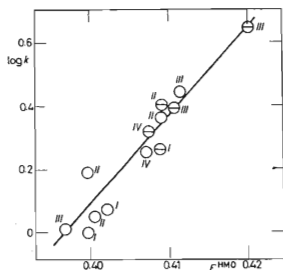

FIG. 4

Plot of Logarithms of Partial Rate Factors of Radical Phenylation[3,16,17] of Bases $I-IV$ against Free Valences Calculated by HMO Method $(N_{max} = \sqrt{3}$, hyperconjugation model of methyl group)
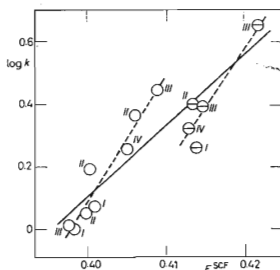
FIG. 5

Plot of Logarithms of Partial Rate Factors of Radical Phenylation[3,16,17] of Bases $I-IV$ against Free Valences Calculated by Pople's SCF Method

$N_{max} = \sqrt{3}$, hyperconjugation model of methyl group. Positions: $\alpha \ominus$, β and $\gamma \circ$.

ment with experimental data (*cf.* refs[19,20]). Furthermore, the experimental data are partially divided into those corresponding to positions in the vicinity of the nitrogen heteroatom (α) and those for the other positions ($\log k(\alpha) = 37 \cdot 14 F^{SCF} - 15 \cdot 02$; $r = 0 \cdot 9085$ for 5 couples and $\log k(\beta, \gamma) = 39 \cdot 99 F^{SCF} - 15 \cdot 91$; $r = 0 \cdot 9570$ for 8 couples).*

Evidently better results are obtained with SCF indices in the case of phenylations taking place in acidic medium[18], in which the substitutions of the forms $I \cdot H^+$ —

TABLE IV

π-Electron Densities on Methyl Groups in SCF Models of Methylpyridines $II-IV$ and Their Protonated Forms $II \cdot H^+ - IV \cdot H^+$

Compound	$q_{C(H_3)}$	$q_{H_3(C)}$	Δq	$\log k^a$
II	$1 \cdot 120$	$0 \cdot 870$	$0 \cdot 250$	$7 \cdot 73$
$II \cdot H^+$	$1 \cdot 120$	$0 \cdot 869$	$0 \cdot 251$	—
III	$1 \cdot 120$	$0 \cdot 876$	$0 \cdot 244$	$5 \cdot 62$
$III \cdot H^+$	$1 \cdot 121$	$0 \cdot 875$	$0 \cdot 246$	—
IV	$1 \cdot 122$	$0 \cdot 869$	$0 \cdot 253$	$8 \cdot 88$
$IV \cdot H^+$	$1 \cdot 123$	$0 \cdot 868$	$0 \cdot 255$	—

[a] Logarithm of rate constant of protodetritiation with the mixture sodium methylate–methanol (White and Lazdins[7]).

TABLE V

Comparison of the Basicity of Compounds $I-IV$ with the SCF and HMO Data

Base	$pK_a{}^a$	$pK_a{}^b$	q_N^{SCF}	$q_{N^+}^{SCF}$	q_N^{HMO}	$q_{N^+}^{HMO}$	ΔW^{SCF} (eV)	ΔW^{HMO} (β)
I	$5 \cdot 30$	$5 \cdot 17$	$1 \cdot 2252$	$1 \cdot 249$	$1 \cdot 195$	$1 \cdot 622$	$0 \cdot 1829$	$2 \cdot 149$
II	$5 \cdot 95$	$5 \cdot 97$	$1 \cdot 2301$	$1 \cdot 255$	$1 \cdot 216$	$1 \cdot 635$	$0 \cdot 1831$	$2 \cdot 175$
III	$5 \cdot 85$	$5 \cdot 68$	$1 \cdot 2263$	$1 \cdot 250$	$1 \cdot 194$	$1 \cdot 621$	$0 \cdot 1820$	$2 \cdot 147$
IV	$6 \cdot 10$	$6 \cdot 02$	$1 \cdot 2298$	$1 \cdot 254$	$1 \cdot 209$	$1 \cdot 631$	$0 \cdot 1810$	$2 \cdot 167$

[a] Ref.[21]. [b] Ref.[22].

* It cannot be ruled out that the mentioned splitting of data F^{SCF} is the consequence of the different value of N_{max} in Coulson's definition of free valence for positions α.

FIG. 6

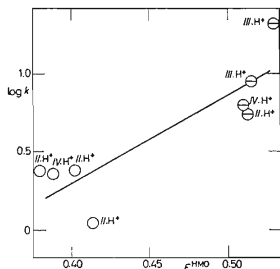Plot of Logarithms of Partial Rate Factors of Radical Phenylation[18] of Ions $I \cdot H^+ -- IV \cdot H^+$ against Free Valences Calculated by HMO Method

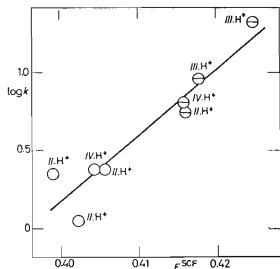$N_{max} = \sqrt{3}$, hyperconjugation model of methyl group.

FIG. 7

Plot of Logarithms of Partial Rate Factors of Radical Phenylation[18] of Ions $I \cdot H^+ -- IV \cdot H^+$ against Free Valences Calculated by Pople's SCF Method

$N_{max} = \sqrt{3}$, hyperconjugation model of methyl group. Positions: $\alpha \ominus$, β and $\gamma \circ$.
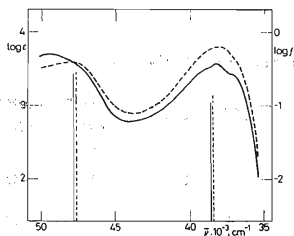

FIG. 8

Comparison of Electronic Spectrum of 3-Methylpyridine (III) with Theoretical Data Calculated by LCI-SCF-MO-LCAO Method

Data for free base III are represented by full lines, those for protonated form $III \cdot H^+$ by broken lines.
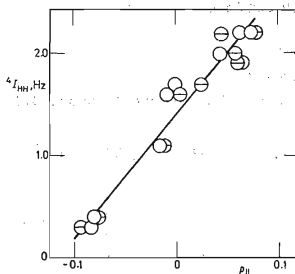

FIG. 9

Plot of Proton Coupling Constants of meta-Interaction in PMR Spectra of Pyridine Bases[23] $I-IV$ against Corresponding π-Bond Orders

$\circ$ SCF data, $\ominus$ HMO data.

$-IV$. H^+ are to be expected (log $k = 42.54 F^{SCF} - 16.85$; $r = 0.9400$ and log $k = 5.48 F^{HMO} - 1.91$; $r = 0.8270$ for 8 couples, see Figs 6 and 7). The values of the F^{HMO} and F^{SCF} used are given in Table III.

The difference between the calculated values of formal π-electron density on the carbon atom and on the hydrogen atoms of methyl group $\Delta q = q_{C(H_3)} - q_{H_3(C)}$ was considered in previous paper[4] as the index describing the liability of these groups to prototropic transformations; the reactivity of methyl groups is expected to decrease in the order $II > IV > III$. In recent kinetic studies[7] of protodetritiation of methylpyridines $II-III$ the following sequence was established: $IV > II > III$. This sequence is in harmony with that predicted by Δq values calculated by SCF method (Table IV).

Basicity

In Table V are compared pK_a values for bases $I-IV$ (refs[21,22]) with π-electron densities on the heteroatoms, q_N and q_{N^+}, and with the differences between the π-electron energies of protonated and unprotonated forms $\Delta W = W^+ - W$. It is evident that only the values of q_N^{SCF} and $q_{N^+}^{SCF}$ are in harmony with the experimental finding that methylpyridines $II-IV$ exhibit higher basicity than the parent compound (I). If one allows for a possible steric effect of methyl group in 2-methylpyridine (II) on the pK_a value, the sequence of the SCF densities compares well with experimental data.

Physical Properties

Electronic spectra. The electronic spectra of aqueous solutions of compounds $I-IV$ measured in the neutral and acidic medium exhibit two absorption bands which can be assigned to $\pi \rightarrow \pi^*$ transitions of the heteroaromatic π-sextet. The comparison of the experimental with the theoretical data obtained by LCI method using SCF-MO is presented in Table VI. Is is evident that the theoretical data account well for the following experimental facts: *a*) a weak red shift of the maxima of both absorption bands brought about by introduction of methyl group on the pyridine ring, and *b*) low sensibility of the positions of the bands towards the substituent position and protonation. Graphical comparison of the course of the extinction curves for 3-methylpyridine (III) and its protonated form $III . H^+$ with LCI data is represented in Fig. 8. Summarizing, it can be stated that the better agreement is achieved between the theoretical and experimental energies than between the analogical intensity data (Table VI). Similarly to the pyridine (I) and its cation $I . H^+$, the single electron transition between frontier MO's $1 \rightarrow 1'$, *i.e.* the $N \rightarrow V_1$ transition, is of the greatest weight in the lowest frequency band in the electronic spectra of methylderivatives $II-IV$ and $II . H^+ - IV . H^+$. This fact may, at least, to a certain extent, account for the finding that in case of methylpyridines there

Theoretical and Experimental Electronic Spectra of Methylpyridine *I—IV* and Their Protonated Forms *I*. H⁺ — *IV*. H⁺

Symbols used: E band maximum energy, ε molar absorptivity, f oscillator strength.

Compound	LCI-SCF-MO calculation				Experiment[a]	
	E	$\log f$	$i - j$[b]	%[c]	E	$\log \varepsilon$
I	39·29	−1·237	1 — 1′	69·68	38·99	3·470
			2 — 2′	30·09		
	50·17	−2·518	1 — 2′	54·64	50·76	3·643
			2 — 1′	45·16		
I. H⁺	39·21	−1·160	1 — 1′	71·56	39·29	3·750
			2 — 2′	28·19		
	49·85	−3·590	2 — 1′	51·98	50·00	3·545
			1 — 2′	47·79		
II	38·51	−1·004	1 — 1′	68·05	38·17	3·670
			2 — 2′	21·64		
	47·76	−0·560	1 — 2′	63·88	49·75	3·653
			2 — 1′	22·81		
			1 — 1′	9·90		
II. H⁺	38·37	−0·923	1 — 1′	71·26	38·31	3·899
			2 — 2′	20·32		
	47·62	−0·654	1 — 2′	61·09	49·26	3·614
			2 — 1′	27·93		
			1 — 1′	7·21		
III	38·62	−1·128	1 — 1′	64·08	38·10	3·583
			2 — 2′	20·63		
			2 — 1′	5·48		
	47·55	−0·590	1 — 2′	62·46	49·75	3·690
			2 — 1′	23·75		
			1 — 1′	12·47		
III. H⁺	38·52	−1·051	1 — 1′	66·93	38·02	3·804
			2 — 2′	19·39		
			2 — 1′	4·86		
	47·43	−0·674	1 — 2′	59·90	48·31	3·601
			2 — 1′	28·25		
			1 — 1′	10·51		
IV	38·87	−1·320	1 — 1′	66·80	39·45	3·400
			2 — 2′	26·51		
			3 — 2′	5·51		
	47·12	−0·522	2 — 1′	87·05	49·38	3·635
			1 — 2′	11·32		
IV. H⁺	38·81	−1·230	1 — 1′	68·94	39·76	3·691
			2 — 2′	24·59		
			3 — 2′	5·45		
	46·54	−0·478	2 — 1′	89·21	46·30	3·822
			1 — 2′	9·30		

*   See note on the following page.

is a certain interrelation between the position of this band and the excitation energy $E(N \rightarrow V_1)$ calculated by the HMO method (see Fig. 6 in the work[4]).

PMR *spectra*. Similarly as in cases mentioned previously[4] there exists a parallel change in the values of π-electron densities, q^{SCF} and q^{HMO}, with the values of proton chemical shifts in the corresponding positions of compounds $II-IV$ which can be described by the following empirical correlations (for 10 couples):

$$\tau \,(\text{p.p.m.}) = 13 \cdot 20 q^{SCF} \ - 10 \cdot 36 \;; \quad r = 0 \cdot 9830 \,,$$

$$\tau \,(\text{p.p.m.}) = 15 \cdot 89 q^{HMO} \ - 13 \cdot 15 \;; \quad r = 0 \cdot 9212 \,.$$

Similar correlations can be also obtained for all the spin-spin coupling contants J_{HH} and π-bond orders p^{SCF} and p^{HMO}, for compounds $I-IV$ (for 22 couples)*:

$$J_{HH}(\text{Hz}) = 6 \cdot 2 p^{SCF} \ + 2 \cdot 0 \;; \quad r = 0 \cdot 9085 \,,$$

$$J_{HH}(\text{Hz}) = 6 \cdot 3 p^{HMO} \ + 2 \cdot 0 \;; \quad r = 0 \cdot 9079 \,.$$

It is noteworthy that within single groups of interaction constants a quite different situation may be found. So, the changes in the values of $^3J_{HH}$ (*ortho*) or $^5J_{HH}$ (*para*) have no analogy in the change of π-bond orders, while the changes in $^4J_{HH}$ (*meta*) follow closely the above π-electron characteristics, as evident from Fig. 9 ($^4J_{HH}$ (Hz) = = $11 \cdot 9p + 1 \cdot 4$; for 10 couples $r = 0 \cdot 9808$ for SCF data and $r = 0 \cdot 9692$ for HMO ones). In all cases the experimental data reported by Brügel[23] were used.

CONCLUSION

The results presented in this paper show that semiempirical HMO and SCF calculations of methylpyridines provide in many respects nearly equivalent data; the similar situation was already found with the cyanoderivatives of pyridines[24]. The interpretation of chemical reactivity of compounds $II-IV$ is improved by the use of SCF method only in cases where the ions $II \cdot H^+ - IV \cdot H^+$ participate in reactions and

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* The π-bond orders were considered also for non-adjacent atom centers. The same approach was already used in the work[24].

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[a] Measured on a Optica Milano CF 4NI Spectrophotometer using 10^{-4}M solutions of the free bases $I-IV$ in water and of the protonated forms in 0·2N sulphuric acid. [b] Transition between the i-th and j-th MO's (see Table II). [c] Weights of configurations in excited states (included only those higher than 5%).

further in estimating prototropic reactivity of methyl groups on the basis of π-electron densities.

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