

HYPERCONJUGATIVE EFFECT IN METHYL PYRIDINES

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ABSTRACT

The hyperconjugative effect of methyl group in γ -picoline, 2 : 6-lutidine and 2 : 4 : 6-collidine has been calculated by the conventional molecular orbital method. It has been concluded that both hyperconjugative and inductometric effects play their rôle in determining the physico-chemical properties of these systems.

From time to time attempts have been made by the theoretical chemists to interpret the interesting physico-chemical properties of methyl pyridines. Introduction of each methyl group in the α -position increases the pK_a of pyridine by about 0.73 and in the γ -position by about 0.82. But the introduction of two methyl groups in α -positions increases the pK_a by $2 \times 0.73 - 0.06$. β -picolines show unusual acidity and are much less prototropically active compared with other methyl pyridines.

Brown and Murphy (1951) found that the prototropic reactivity of β -picoline lies between toluene on the one hand and other picolines on the other. They postulate a direct meta-interaction in these systems, in which the non-bonding lone pair electrons of nitrogen were placed in the first anti-bonding molecular orbital of pyridine. Later on Brown and Dewar (1953) showed that meta-interaction effect was not very satisfactory. Taking into consideration the inductometric effect of the electron releasing methyl group they succeeded in explaining the basicities of the various methyl pyridines, but admitted that other chemical characteristics could not be explained by their method. Löwdin (1951) made a theoretical calculation of the dipole moment of various picolines considering the introduction of a methyl group as a perturbation which changed the coulomb integral of the carbon atom to which the methyl group was attached. All these workers, however, overlooked the possibility of any hyperconjugative effect that may be operative in these systems.

It has been known for a long time that methyl group has a peculiar electron releasing property and, when present in a compound, tends to introduce incipient unsaturation into the system. This was called Baker-Nathan effect, but is popularly known as 'hyperconjugation', the name suggested by Mulliken. Mulliken, Rieke and Brown (1941) computed the hyperconjugation energy and bond orders of a number of methylated compounds by conventional molecular orbital method. Coulson and Crawford (1953) extended and further developed the idea in their calculation of orbital energies, electron densities, etc. of toluene and other methylated benzenes. In their treatment the H_3 of the methyl group was treated as a hetero-atom. The $1s$ electrons of the three hydrogen atoms were assumed to act together, behaving like one π -electron on a nucleus having a coulomb integral different from that of carbon atom. This virtual π -electron was then assumed to undergo mesomeric interaction with the real π -electron system of the phenyl ring. Thus, in short, the hyperconjugative effect may be considered as an effective σ - π interaction. This

treatment has been very successful in explaining the characteristic chemical reactivities of methylated benzenes, from both the points of view of 'isolated atom' and 'localization' theory.

In the present paper the rôle of hyperconjugation effect in determining the characteristic properties of methyl pyridines has been estimated by established theoretical methods. As far as we are aware, this effect has been completely ignored in all previous calculations.

METHOD OF CALCULATION

In the present calculation the method suggested by Coulson and Crawford (1953) was closely followed. As the experimental values for the bond lengths are not available, no overlap correction was introduced. Various coulomb and resonance parameters used in the calculation are given below:

Coulomb integral for $N = E_0 + 0.66\beta$	Resonance integral for C-C bond = β
" " " $H_3 = E_0 - 0.50\beta$	" " " C-N " = β
" " " C = $E_0 - 0.10\beta$ (attached to H_3)	" " " C- H_3 " = 2.5β
" " " C = $E_0 + 0.0825\beta$ (attached to N)	" " " C-C " = 0.7β (adjacent to H_3)
" " " C = E_0	

With these parameters secular equations were set up in the usual way, the determinant being reduced by C_{2v} symmetry operation and finally solved for the energy values which were used in the calculation of electron densities, resonance and hyperconjugation energies.

RESULTS

The orbital energies calculated in this way for γ -picoline, 2 : 6-lutidine and 2 : 4 : 6-collidine are given in Table I.

TABLE I
M.O. energies for methyl pyridines in unit of $(E - E_0)/\beta$

Pyridine	γ -Picoline	2 : 6-Lutidine	2 : 4 : 6-Collidine
2.1837	2.4349	2.5400	2.5717
1.2225	2.0936	2.3549	2.3598
1.0420	1.1520	1.9294	2.3549
-0.7694	1.0421	1.2089	1.8750
-0.9598	-0.7630	0.9650	1.1460
-1.8940	-0.9604	-0.7630	0.9650
	-1.8580	-0.9420	-0.7571
	-2.9170	-1.8490	-0.9420
		-2.8954	-1.8139
		-2.9237	-2.8954
			-2.9000
			-2.9390

In Table II are given the resonance energies, overall hyperconjugation energies and hyperconjugation energy per methyl group for these systems.

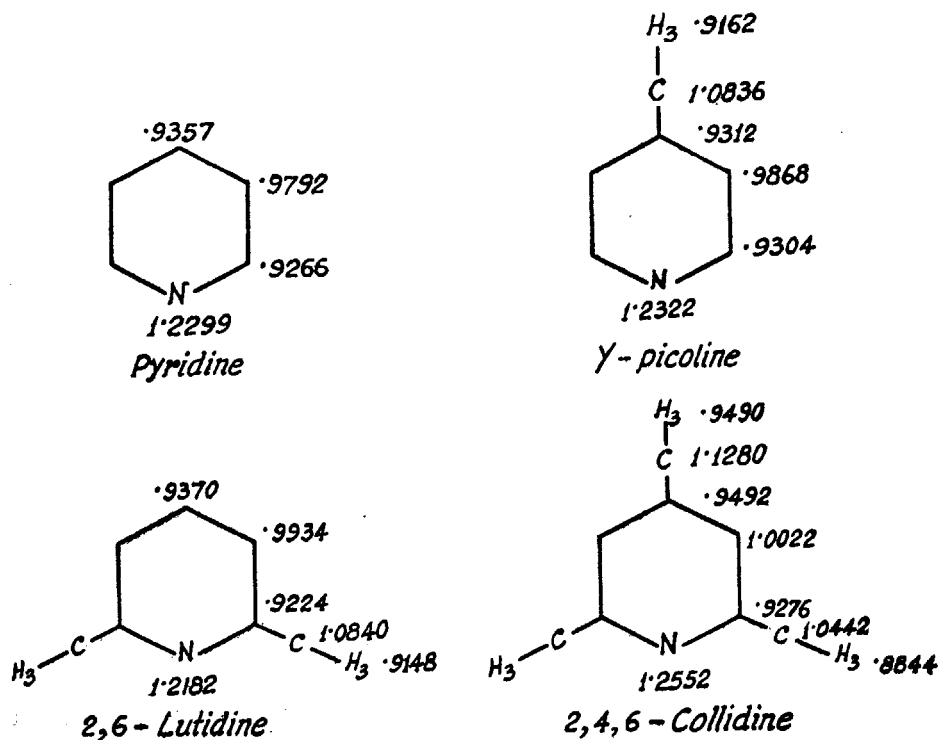
TABLE II
Resonance and hyperconjugation energies

Compound	Resonance energy (β)	Hyperconjugation energy (β)	Hypercon. energy per methyl group (β)
Pyridine ..	2.1302	—	—
γ -picoline ..	2.2630	0.1328	0.1328
2 : 6-lutidine ..	2.3982	0.2680	0.1340
2 : 4 : 6-collidine	2.5306	0.4004	0.1334

Calculated electron densities are shown against each atom of the respective compound in Text-fig. 1.

DISCUSSION

From Table II it is evident that as the number of methyl groups is increased, the resonance and hyperconjugation energies increase, which accounts for the extra stabilization of these systems over pyridine. The hyperconjugation energy per methyl group is, however, more or less constant. The hyperconjugative effect of methyl group calculated from pyridine compounds appears to be higher than that calculated by Coulson and Crawford (1953) for phenyl compounds. A comparison, however, is not justified as Coulson and Crawford's calculation was subjected to overlap correction which is known to lower the absolute magnitude of the various energy quantities.



TEXT-FIG. 1. Electron Density.

From Text-fig. 1 it is evident that all these compounds are susceptible to cationoid attack at the β -position just like pyridine itself. This is clearly borne out by the experimental observation. The electron density at H_β is less than unity in all the methylated compounds, which evidently makes these positions rather susceptible to anionoid attack. In fact, methyl group is smoothly oxidized to carboxyl group in all these compounds, the α -positions being particularly reactive.

The ionization potentials of methyl pyridines are only slightly different from those of pyridine. Introduction of methyl groups into phenyl ring on the other hand appreciably lowers the ionization potential of benzene. These facts have been interpreted on the assumption that in phenyl compounds potentials refer to π -ionization, while in pyridines to n -ionization, i.e. ionization of non-bonding lone pair electrons of the nitrogen atom. The π -ionization potentials may be theoretically calculated from the energy of the topmost filled molecular orbital of the respective compound. From Table I it is evident that the introduction of methyl groups into pyridine alters the energy of the topmost filled π -orbital only slightly. Therefore even the π -ionization potential is not expected to change much on methyl substitution. It may be concluded that no change in the ionization potential of pyridine on methyl substitution can be taken as an indication that the ionization refers to n -electron.

In Table III are summarized the energy changes associated with the first $\pi \rightarrow \pi^*$ transition in various methyl pyridines.

TABLE III
Excitation energy in methyl pyridines

Compound	$\pi \rightarrow \pi^*$ transition energy in unit of β
Pyridine	0.2726
γ -picoline	0.2791
2 : 6-lutidine	0.2020
2 : 4 : 6-collidine	0.2079

It is evident that the usual red shift in the $\pi \rightarrow \pi^*$ absorption associated with methyl substitution in phenyl series is not observable in the pyridine series from the consideration of hyperconjugation.

In Table IV are summarized the values of electron density in the nitrogen atom and the pK_a value of the respective methyl pyridines.

TABLE IV
Electron density and basicity

Compound	Electron density (e)	pK_a
Pyridine	1.2299	5.17
γ -picoline	1.2322	6.02
2 : 6-lutidine	1.2182	6.51
2 : 4 : 6-collidine	1.2552	7.62

It is evident that there is no systematic correlation between the electron density and pK_a values in the methyl pyridine systems. It was noticed by Longuet-Higgins and Coulson (1949) that no such correlation exists for aza-hydrocarbons,

like pyridine, quinoline, iso-quinoline, etc. Brown and Dewar (1953), however, have shown from the consideration of inductometric effect that such a correlation does exist in methyl pyridine systems.

From all these considerations it may be concluded that the physico-chemical properties of methyl pyridines are determined by the joint contribution of inductometric and hyperconjugative effect, and one cannot be considered divorced from other.

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