31. Photoelectron Spectra of Azabenzenes and Azanaphthalenes: III. The Orbital Sequence in Methyl- and Trimethylsilyl-Substituted Pyridines[1])

by **E. Heilbronner**[2]), **V. Hornung**[2]), **F. H. Pinkerton**[3]) and **S. F. Thames**[3])

Physikalisch-Chemisches Institut der Universität Basel and
Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Miss.

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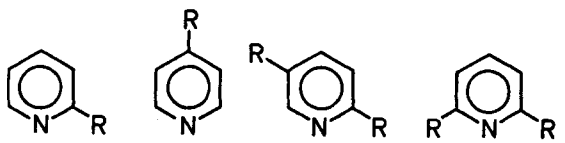
Summary. The ionization potentials of methyl-, *t*-butyl- and trimethylsilyl-substituted pyridines have been determined by high-resolution photoelectron spectroscopy. The results are discussed in terms of destabilizing inductive and stabilizing conjugative effects of the substituents, and have been parametrized on the basis of a HMO-type perturbation treatment. Our data are in accord with the idea that the topmost occupied orbital in pyridine is a 'lone pair' orbital.

Some time ago [2] we have shown that the photoelectron spectrum of 2-trimethylsilyl-pyridine (VI) could be interpreted in terms of two effects,

(a) an inductive effect of the trimethylsilyl group which raises the orbital energies of σ- (*e.g.* lone pair) and of π-orbitals (*cf.* [3]),

(b) a Si$\leftarrow\pi$ back-donation effect which lowers the π-orbital energies and thus tends to compensate (a) (*cf.* [4]).

We now present further experimental results which support this interpretation and allow a parametrization of the underlying molecular orbital model. Our new results also provide additional evidence that in the parent compound pyridine (I) the lone-pair orbital $11\mathbf{a}_1(\sigma)$ lies above the highest occupied π-orbital $1\mathbf{a}_2(\pi)$, a point about which there has been some controversy [2] [5] [6] [7] [8].



R				
H	I			
Me	II	III	IV	V
$Si(Me)_3$	VI	VII	VIII	IX
$C(Me)_3$		X		

Table 1 contains the experimental results. The bands in the photoelectron spectra (*cf.* Fig. 1) are numbered according to increasing ionization potentials. Multiple bands, recognizable by their increased integrated intensity, have been separated into their components. The resulting ionization potentials, which are affected with wider confidence limits, are given in italics.

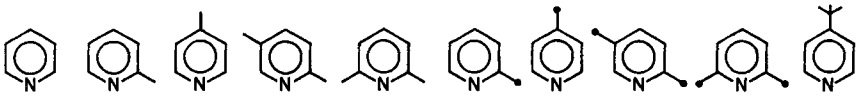
[1]) Part 30 of 'Applications of Photoelectron Spectroscopy'; Part 29: [1].

[2]) Basel.

[3]) Hattiesburg, Miss. 39401, USA.

Table 1. *Vertical Ionization Potentials* $I_{v,J}$ *in eV*

Values given in *italics* have been obtained by deconvolution. All values have been rounded to the nearest ± 0.05 eV or ± 0.1 eV.

	I	II	III	IV	V	VI	VII	VIII	IX	X	
Formula[a]											
J = ①	9.60	9.20	9.50	8.80	8.90	8.90	*9.30*	8.65	8.50	*9.30*	n[b]
②	9.75	*9.50*	9.60	9.25	*9.30*	*9.30*	*9.40*	8.95	8.95	*9.45*	$\pi(1\mathbf{a}_2)$[b]
③	10.50	10.25	10.05	10.00	10.05	10.10	9.90	9.5	9.85	9.70	$\pi(2\mathbf{b}_1)$[b]
④		12.6	12.1	12.2	12.1	(10.5)	11.0	9.8	10.4	11.2	
⑤		13.1	12.8	13.8	12.9		12.2	10.1	11.5	12.6	
⑥		14.0	13.1	14.8	13.9		12.9	10.8		14.2	
⑦		15.2	14.3	16.1	14.8		13.3			14.7	
⑧		16.0	(15.4)[c]		(16.0)		14.2			15.4	
⑨		16.7	(15.9)				(15.1)				

a) -- = methyl; —● = trimethylsilyl; —≮ = *t*-butyl.
b) The correlation lines are those of Fig. 2, 3 and 4.
c) Values in parentheses refer to recognizable maxima in strongly overlapping σ-bands.

The orbital correlation diagrams of Fig. 2, 3, and 4 summarize our assignment for the three highest occupied molecular orbitals of compounds I to X.

This assignment can be derived on the basis of a simple HMO-model, assuming the validity of *Koopmans*'s theorem [9], *i.e.*

$$\varepsilon(\psi_J) = -I_{v,J} \tag{1}$$

(where $\varepsilon(\psi_J)$ is the orbital energy associated with a molecular orbital ψ_J and $I_{v,J}$ the corresponding vertical ionization potential), even though molecular orbital models which assume σ/π-separation yield unreliable charge distributions in the case of azabenzenes [10]. For the π-orbitals of I we use the simple HMO model suggested by an investigation of the PE. spectra of azabenzenes and azanaphthalenes [1] [11].

This model is characterized by the set of parameters $\beta_{\mu\nu} = \beta$ for all π-bonds, $\alpha_N = \alpha + \beta$ for the *Coulomb* integrals of the nitrogen atom and $\alpha_{ortho} = \alpha + \beta/3$ for the carbon atoms in *ortho*-position to it [1]. The relevant results are summarized in Table 2. We restrict ourselves to the lowest π-states $^2\mathbf{A}_2$ and $^2\mathbf{B}_1$ of the pyridine radical cation I^+ (*i.e.* those corresponding to ejection of an electron from $\psi_J = 1\mathbf{a}_2(\pi)$ or $\psi_J = 2\mathbf{b}_1(\pi)$), as it has been shown [1] that the model yields unreliable results for the lower lying π-orbital $1\mathbf{b}_1(\pi)$.

The influence of substituents R on the orbital energies $\varepsilon(\psi_J)$ and thus on the positions $I_{v,J}$ of the bands in the PE. spectra is dealt with by a simple perturbation treatment.

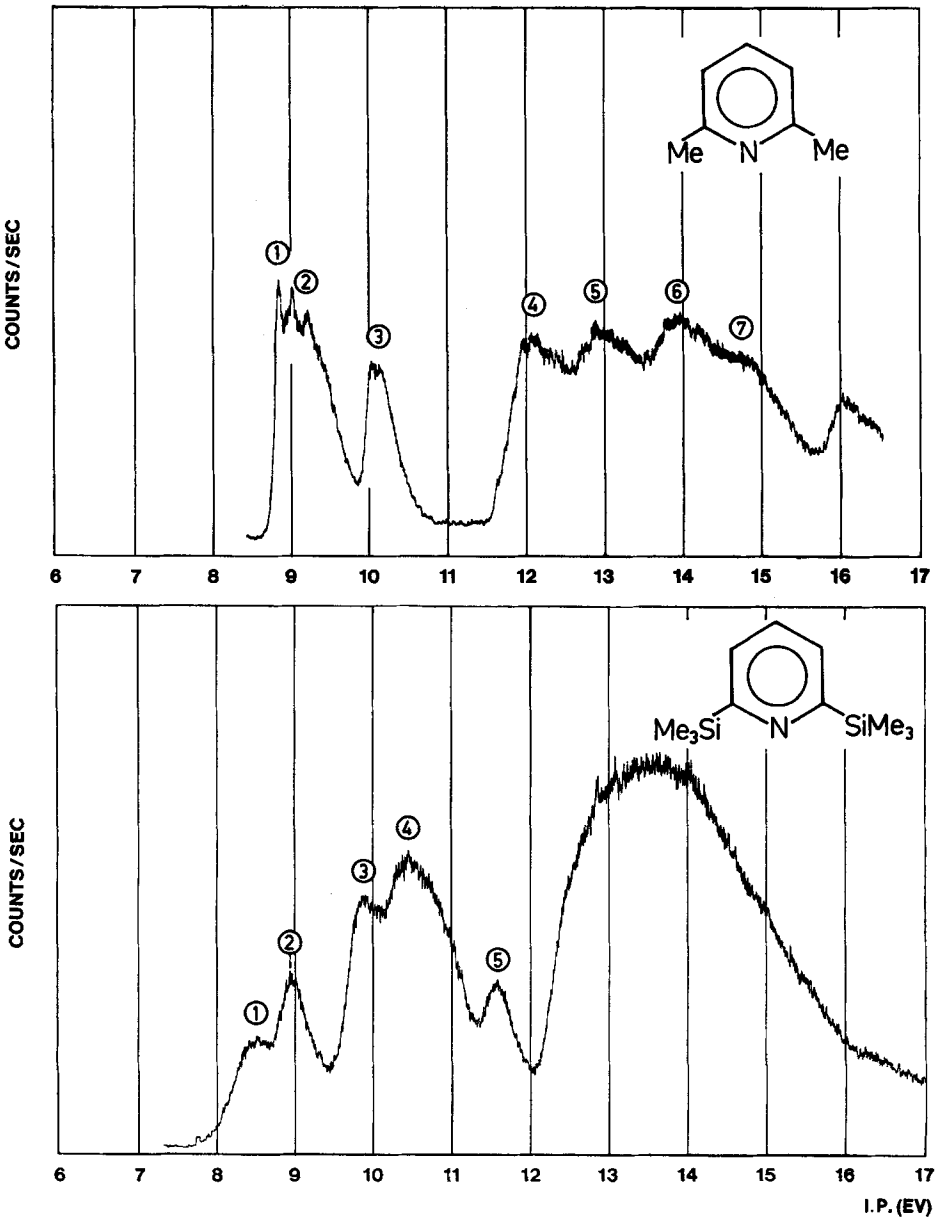


Figure 1. *PE.-spectra of 2,6-dimethylpyridine (V) and 2,6-bis-trimethylsilyl-pyridine (IX).*
The numbers (J) refer to the ionization potentials listed in Table 1.

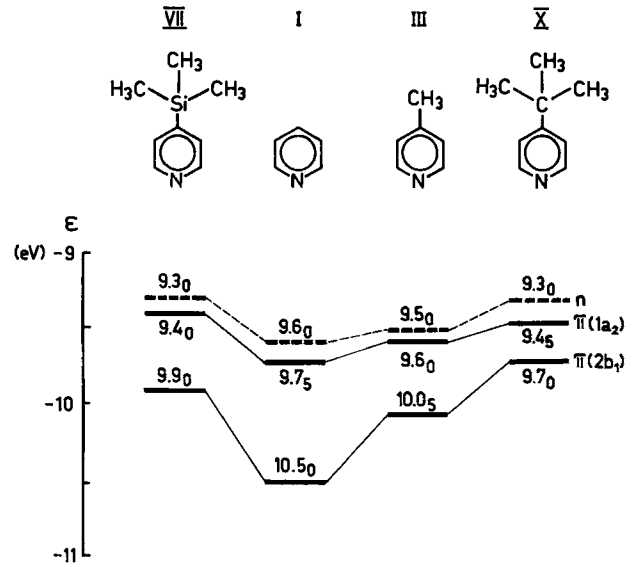


Figure 2. *Correlation diagram for the three highest occupied orbitals of* para-*substituted pyridines*
The orbital labels $1a_2$ and $2b_1$ given in brackets refer to the parent compound I

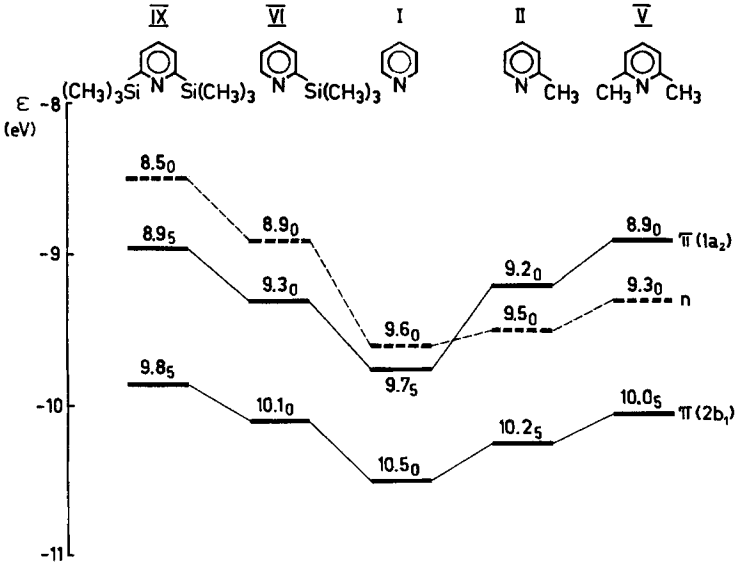


Figure 3. *Correlation diagram for the three highest occupied orbitals in* ortho-*substituted pyridines*
The orbital labels $1a_2$ and $2b_1$ given in brackets refer to the parent compound I

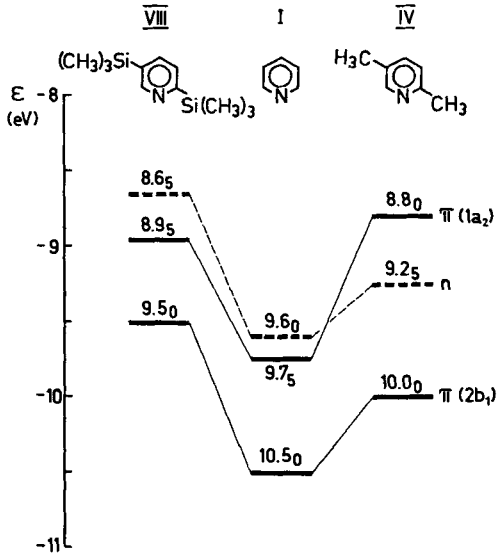
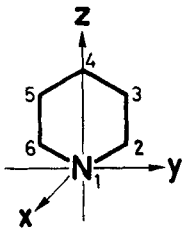


Figure 4. *Correlation diagram for the three highest occupied orbitals in 2,5-disubstituted pyridines*
The orbital labels $1\mathbf{a}_2$ and $2\mathbf{b}_1$ given in brackets refer to the parent compound I

Table 2. *HMO-Model for the π-Orbitals of Pyridine (I)*
Parameters: $\beta_{\mu\nu} = \beta$; $\alpha_N = \alpha + \beta$; $\alpha_{ortho} = \alpha + \beta/3$



Orbitals: Coefficients $C_{J\mu}$

ψ_J	μ = 1	2	3	4
$1\mathbf{a}_2(\pi)$	0.0000	0.2911	0.2089	0.0000
$2\mathbf{b}_1(\pi)$	0.2448	0.0063	0.1731	0.3963

Configurations: Charge Orders q_μ

	q_1	q_2	q_3	q_4
$^1\mathbf{A}_1$	1.2838	0.9841	0.9226	0.9028
$^2\mathbf{A}_2$	1.2838	0.6930	0.7137	0.9028
$^2\mathbf{B}_1$	1.0391	0.9778	0.7495	0.5064

Let ϕ_ξ be the $2p$ atomic orbital at the position ξ of substitution and ϕ_ϱ an atomic or group orbital of R having the proper symmetry to interact with ϕ_ξ. The exact nature of ϕ_ϱ is left unspecified for the moment. The perturbation operator $\mathbf{h}$ is defined by the list

$$\begin{aligned} \langle \phi_\xi | \mathbf{h} | \phi_\xi \rangle &= \delta\alpha(\mathrm{R}) \\ \langle \phi_\xi | \mathbf{h} | \phi_\varrho \rangle = \langle \phi_\rho | \mathbf{h} | \phi_\xi \rangle &= \varkappa(\mathrm{R}) \\ \langle \phi_\mu | \mathbf{h} | \phi_\nu \rangle &= 0 \text{ in all other cases.} \end{aligned} \tag{2}$$

Under these conditions the change $\delta\varepsilon(\psi_J)$ in the orbital energy $\varepsilon(\psi_J)$ is given by

$$\begin{aligned} \delta\varepsilon(\psi_J) &= C_{J\xi}^2\, \delta\alpha(\mathrm{R}) + \frac{[C_{J\xi}\, \varkappa(\mathrm{R})]^2}{\varepsilon(\psi_J) - \varepsilon(\phi_\rho)} \\ &= \left(\delta\alpha(\mathrm{R}) + \frac{\varkappa^2(\mathrm{R})}{\varepsilon(\psi_J) - \varepsilon(\phi_\rho)}\right) C_{J\xi}^2 \end{aligned} \tag{3}$$

where $\varepsilon(\phi_\varrho)$ is the orbital energy associated with ϕ_ϱ. It is immediately apparent that this model, *i.e.* the one defined by the list (2), does *not* allow a separation of inductive ($\delta\alpha(\mathrm{R})$) and conjugative ($\varkappa(\mathrm{R})$) effects. In close analogy to the treatment of I mentioned before, we therefore extend the list (2) defined $\mathbf{h}$ by

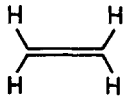
$$\langle \phi_\tau | \mathbf{h} | \phi_\tau \rangle = m\, \delta\alpha(\mathrm{R}) \tag{4}$$

where τ is a position *ortho* to ξ, *i.e. ortho* to the substituent R. The parameter m is an as yet unspecified positive constant: $m < 1$. This leads to

$$\delta\varepsilon(\psi_J) = \frac{C_{J\xi}^2}{\varepsilon(\psi_J) - \varepsilon(\phi_\varrho)}\, \varkappa^2(\mathrm{R}) + (C_{J\xi}^2 + m\,(C_{J\tau}^2 + C_{J\tau'}^2))\, \delta\alpha(\mathrm{R}) \tag{5}$$

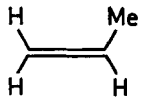
so that a separation of conjugative and inductive effects should in principle become possible. But the set of simultaneous equations derived from (5) and (1) for the set of compounds I to X yields an ill-conditioned regression problem for the determination of the parameters $\delta\alpha(\mathrm{R})$ and $\varkappa(\mathrm{R})$, in that small changes in the experimental values $\delta I_{v,J} = -\delta\varepsilon(\psi_J)$ lead to large errors in the parameters.

For this reason we proceed as follows: we determine first the inductive perturbation parameter $\delta\alpha(\mathrm{CH_3})$ of a methyl group on the basis of the known π-ionization potentials of the hydrocarbons XI to XIX under the implicit assumption that the methyl group does not yield a conjugative contribution towards $\delta\varepsilon(\psi_J)$, *i.e.* $\varkappa(\mathrm{CH_3}) = 0$. (The numbers attached to the following formulae are the vertical ionization potentials in eV.)



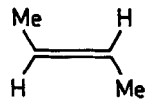
XI

10.51 [8]



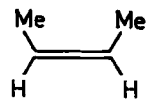
XII

9.73 [8]



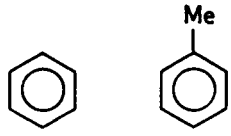
XIII

9.12 [12]



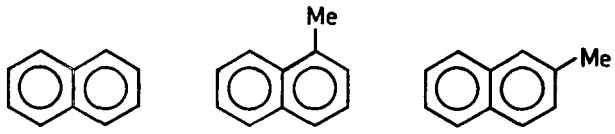
XIV

9.12 [12]



XV 9.24 [8]

XVI 8.82 [8]



XVII
8.15 [1] [13]
8.88
10.00

XVIII
7.95 [14]
8.74
9.68

XIX
7.93 [14]
8.63
9.83

Table 3 contains the experimental values for the shifts

$$\delta I_{o,J} = I_{v,J}(\text{methyl derivative}) - I_{v,J}(\text{parent compound})$$

$$= -\delta\varepsilon(\psi_J) \tag{6}$$

and those of the independent parameter

$$a_J = \sum_{\xi} (3\, C_{J\xi}^2 + C_{J\tau}^2 + C_{J\tau'}^2)/3, \tag{7}$$

obtained according to (5) under the implicit assumption $m = 1/3$ for the set of compounds XI to XIX, together with the shifts $\delta I'_{v,J}$ calculated from the least-squares regression line (degree of freedom = 8)

$$-\delta I'_{v,J} = 0.0528 + 1.0110\, a_J; \text{ (correlation coefficient } r = 0.9973). \tag{8}$$

Table 3. *Correlation between the experimental shifts* $\delta I_{v,J}$ *(6) and the perturbation coefficient* $a_J = \Sigma_\xi (3\, C_{J\xi}^2 + C_{J\tau}^2 + C_{J\tau'}^2)/3$ *(7) for methyl-substituted hydrocarbons*[a]

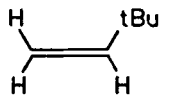
All values in eV. The shifts $-\delta I'_{v,J}$ have been calculated according to (8). $\Delta\sigma I_{v,J} = \delta I_{v,J} - \delta I'_{v,J}$.

	$-\delta I_{v,J}$	a_J	$-\delta I'_{v,J}$	$\Delta\delta I_{v,J}$
XII	0,78	0.67	0.730	−0.050
XIII	1.39	1.33	1.397	+0.007
XIV	1.39	1.33	1.397	+0.007
XVI	0.42	0.39	0.447	+0.027
XVIII	0.20	0.20	0.255	+0.055
	0.14	0.11	0.164	+0.024
	0.32	0.21	0.265	−0.055
XIX	0.22	0.15	0.204	−0.016
	0.25	0.22	0.275	+0.025
	0.17	0.09	0.144	−0.026

[a] The values $C_{J\xi}$ are those obtained from a standard HMO calculation.

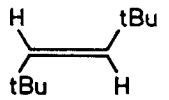
It could be argued that the zero-values for the parent compounds XI, XV, and XVII should be included in the regression calculation. If these five pairs {0;0} (three for XVII!) are included (degree of freedom = 13) one obtains $-\delta I'_{v,J} = 0.0261 + 1.0401\ a_J$ (correlation coefficient $r = 0.9970$) and thus $\delta\alpha(CH_3) = 1.04$ eV. We conclude from the two treatments that the inductive perturbation parameter for a methyl group (excluding conjugation) is $\delta\alpha(CH_3) = 1.0$ eV.

In a similar fashion we assess the inductive parameter $\delta\alpha(t\text{-butyl})$, using the vertical ionization potentials corresponding to ejection from the highest occupied orbitals of the compounds XX to XXV [3] [4], again under the implicit assumption that $\varkappa(t\text{-butyl}) = 0$. (The numbers attached to the following formulae are the vertical ionization potentials in eV).



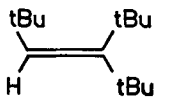
XX

9.62 [15] [16]



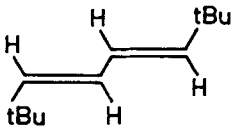
XXI

8.99 [15] [16]



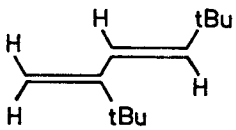
XXII

8.5 [15] [16]



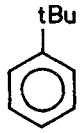
XXIII

8.23 [16]



XXIV

8.22 [16]



XXV

8.60 [17]
9.13

The observed shifts $\delta I_{v,J}$ (see (6)) and the corresponding perturbation parameters a_J (see (7)) (with $m = 1/3$) are given in Table 4. A least-squares analysis, including the four zero pairs {0;0} for the parent compounds ethylene, butadiene and benzene

Table 4. *Correlation between the experimental shifts $\delta I_{v,J}$ (6) and the perturbation coefficient $a_J = \Sigma_\xi(3\,C^2_{J\xi} + C^2_{J\tau} + C^2_{J\tau'})/3$ (7) for t-butyl-substituted hydrocarbons*[a]

All values in eV. The shifts $\delta I'_{v,J}$ have been calculated according to $-\delta I'_{v,J} = 1.19\ a_J \cdot \Delta\delta I_{v,J} = \delta I_{v,J} - \delta I'_{v,J}$.

	$-\delta I_{v,J}$ [b]	a_J	$-\delta I'_{v,J}$	$\Delta\delta I_{v,J}$
XX	0.89	0.67	0.80	−0.09
XXI	1.52	1.33	1.58	+0.06
XXII	2.01	2.00	2.38	+0.37
XXIII	0.85	0.82	0.98	+0.13
XXIV	0.86	0.71	0.84	−0.02
XXV	0.64 [c]	0.39	0.46	−0.18
	0.11 [c]	0.17	0.20	+0.09

a) See footnote of Tab. 3.
b) All values, except those marked [c] taken from [15] [16] [17].
c) Unpublished results.

(twice!), yields the regression line $-\delta I'_{v,J} = 0.0562 + 1.0857\ a_J$ (degree of freedom = 9). If the regression line is constrained to pass through the origin, its slope is 1.19 eV/unit of a_J. This latter value has been used to compute the $\delta I'_{v,J}$ given in Table 4.

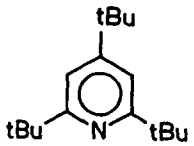
Since the pyridine nucleus is more electronegative than a hydrocarbon system, the perturbation parameters derived for the methyl and *t*-butyl groups are lower limits for those effective in alkyl-substituted pyridines: $\delta\alpha(CH_3) > 1.0$ eV, $\delta\alpha$(*t*-butyl) > 1.2 eV. Furthermore, the results obtained by *Bock et al.* [3] [4] [15] [16] [17] suggest that the inductive effect of a trimethylsilyl group is much larger than that of a *t*-butyl group: $\delta\alpha$(trim.-silyl)$>\delta\alpha$(*t*-butyl). The following analysis confirms these expectations.

Consider first the methyl substituted pyridines II to V. The perturbation factors a_J given in Table 5 have been calculated according to (7) from the squared orbital coefficients given in Tab. 2. Under the assumption $\varkappa(CH_3) = 0$, the observed shifts $\delta I_{v,J} = -\delta\varepsilon(\psi_J)$ (see (6)) yield the least-squares regression line (degree of freedom = 6)

$$-\delta I'_{v,J} = 0.0449 + 1.1522\ a_J;\ \text{(correlation coefficient } r = 0.9263). \tag{9}$$

If one includes the zero-value for I, the regression $-\delta I'_{v,J} = 0.0198 + 1.2012\ a_J$ is obtained (correlation coefficient $r = 0.9596$; degree of freedom = 8). If the regression line is constrained to pass through the origin its slope is 1.26 eV/unit of a_J. For the perturbations $a_J \cdot \delta\alpha(CH_3)$ of Table 5, we assume $\delta\alpha(CH_3) = 1.25$ eV, larger by 0.25 eV than in the case of the hydrocarbons XI to XIX.

The corresponding calibration of $\delta\alpha$(*t*-butyl) is based on the experimental results obtained for X and those given by *Oehling, Schäfer & Schweig* [18] for 2,4,6-tri-*t*-butyl pyridine XXVI (see Table 5).



XXVI 8.6; (8.7); 9.3 [18]

These data yield $\delta\alpha$(*t*-butyl) = 1.5 eV, *i.e.* a value larger by 0.3 eV than that derived from the hydrocarbons XX to XXV.

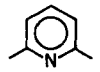
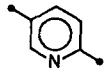
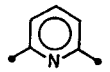
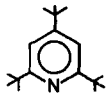
As mentioned already, two opposing effects have to be taken into consideration for the perturbation induced by a trimethylsilyl group: a destabilizing inductive effect $\delta\alpha$(trim.-silyl) and a stabilizing Si$\leftarrow\pi$ back-donation effect. According to (5) $\delta\alpha$(trim-silyl) can be assessed from those ionization potentials which correspond to ejection of an electron from an orbital in which $\Sigma_\xi C^2_{J\xi} = 0$ or $\Sigma_\xi C^2_{J\xi} \approx 0$. As seen from Table 5 this is the case for VI ($2\mathbf{b}_1(\pi)$), VII ($1\mathbf{a}_2(\pi)$), IX ($2\mathbf{b}_1(\pi)$). Comparison of the observed shifts $\delta I_{v,J}$ with the computed factors a_J leads to $\delta\alpha$(trim.-silyl) = 2.4 eV. As expected, this perturbation parameter is much larger than 1.5 eV, the value obtained for $\delta\alpha$(*t*-butyl). We can now compute the destabilizations $a_J \cdot \delta\alpha$(trim.-silyl) given in Table 5 for the compounds VI to IX. The differences (*cf.* Table 5)

$$\frac{b_J\varkappa^2(\text{trim.-silyl})}{\varepsilon(\psi_J) - \varepsilon(\phi_o)} = -\delta I_{v,J} - a_J\,\delta\alpha(\text{trim.-silyl}) \tag{10}$$

Table 5. *Observed* ($\delta I_{v,J}$) *and calculated* ($\delta I_{v,J}$) *shifts of* π*-ionization potentials of substituted pyridines*

All values in eV. Factors a_J from (7). Factors $b_J = \Sigma_\xi C_{J\xi}^2$ · Parameters: $\delta\alpha(CH_3) = 1.25$ eV; $\delta\alpha(t\text{-butyl}) = 1.5$ eV; $\delta\alpha(\text{trim.-silyl}) = 2.4$ eV. $\varkappa^2(\text{trim.-silyl})/(\varepsilon(\psi_J)\text{-}\varepsilon(\phi_\varrho)) = -1.5$ eV. Definition of $\delta I_{v,J}$ see (6). $-\delta I'_{v,J} = \dfrac{\varkappa^2(R)}{\varepsilon(\psi_J) - \varepsilon(\phi_\rho)}\, b_J + a_J \cdot \delta\alpha(R)$. $\Delta\delta I_{v,J} = \delta I_{v,J} - \delta I'_{v,J}$.

For all compounds (II–X, XXVI) the first horizontal line refers to orbital ($1\mathbf{a}_2$), the second one to orbital ($2\mathbf{b}_1$), resp., as indicated in the case of II.

	a)		$-\delta I_{v,J} = \delta\varepsilon(\psi_J)$ exper.	a_J	b_J	$a_J \cdot \delta\alpha(R)$	$\dfrac{b_J\, \varkappa^2(R)}{\varepsilon(\psi_J) - \varepsilon(\phi_\rho)}$	$-\delta I'_{v,J}$	$\Delta\delta I_{v,J}$
II		($1\mathbf{a}_2$)	0.55	0.36	0.29	0.45		0.45	−0.10
		($2\mathbf{b}_1$)	0.25	0.15	0.01	0.19		0.19	−0.06
III			0.15	0.14	0.00	0.18		0.18	+0.03
			0.45	0.51	0.40	0.64		0.64	+0.19
IV			0.95	0.67	0.50	0.84		0.84	−0.11
			0.50	0.45	0.18	0.56		0.56	+0.06
V			0.85	0.72	0.58	0.90		0.90	+0.05
			0.45	0.29	0.01	0.36		0.36	−0.09
VI			0.45	0.36	0.29	0.86	−0.41	0.43	−0.02
			0.40	0.15	0.01	0.36	0.04	0.35	−0.05
VII			0.35	0.14	0.00	0.34	0.00	0.34	−0.01
			0.60	0.51	0.40	1.22	−0.62	0.62	+0.02
VIII			0.80	0.67	0.50	1.61	−0.80	+0.86	+0.06
			0.70	0.45	0.18	1.08	−0.38	+0.81	+0.11
IX			0.80	0.72	0.58	1.73	−0.93	+0.86	+0.06
			0.65	0.29	0.01	0.70	−0.06	+0.69	+0.04
X			0.30	0.14	0.00	0.21		0.21	−0.09
			0.80	0.51	0.40	0.77		0.77	−0.03
XXVI			1.15	0.86	0.58	1.29		1.29	+0.14
			1.20	0.80	0.41	1.20		1.20	0.00

a) — = methyl; —• = trimethylsilyl; ⋖ = *t*-butyl.

are postulated to be due to the conjugative interaction of the pyridine π-system with the orbital(s) ϕ_ϱ of the trimethylsilyl group(s), leading to a stabilization $b_J \cdot \varkappa^2$ (trim.-silyl)/$(\varepsilon(\psi_J) - \varepsilon(\phi_\varrho))$. Comparison of the b_J-values with the differences $-\delta I_{v,J} - a_J \cdot \delta\alpha$ (trim.-silyl) yields $\varkappa^2$ (trim.-silyl)/$(\varepsilon(\psi_J) - \varepsilon\ (\phi_\varrho)) = -1.5$ eV.

The computed shifts $\delta I'_{v,J}$ (Table 5) have been calculated with these parameters assuming $\varepsilon(\psi_J) - \varepsilon(\phi_\varrho)$ constant for all compounds considered. This is probably a reasonable first approximation. The correlation between $\delta I_{v,J}$ and $\delta I'_{v,J}$ is shown in Fig. 5.

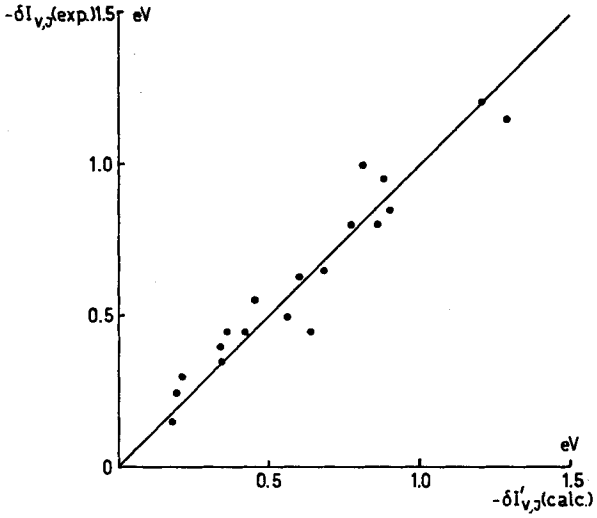


Figure 5. *Comparison of observed* (exp.) *and calculated* (calc.) *substituent induced shifts* $\delta I_{v,J}$ *of* π*-orbital energies*

The corresponding numerical values of $-\delta I_{v,J}$ are given in Table 5

The influence of substitution on the orbital energy $\varepsilon(11\mathbf{a}_1(\sigma))$ of the 'lone pair' orbital $\psi_n \equiv 11\mathbf{a}_1(\sigma)$, the highest occupied orbital of pyridine (I) is postulated to be only inductive [2]. An analysis of the shifts $\delta I_{v,n} = -\delta\varepsilon\ (11\mathbf{a}_1(\sigma)) = -\delta\varepsilon(\psi_n)$ (Table 6) should therefore yield some insight into the degree of delocalization of the 'lone-pair'

Table 6. *Shifts* $-\delta I_{v,J} = \delta\varepsilon(11\mathbf{a}_1(\sigma))$ *of the 'lone pair' orbital energy under the influence of methyl-, t-butyl- and trimethylsilyl substituents*

All values in eV

II	III	IV	V	VI	VII	VIII	IX	X	XXVI
0.10	0.10	0.35	0.30	0.70	0.30	0.95	1.10	0.30	0.90

electrons over the σ-frame of I. Unfortunately our data are too crude to give more than a qualitative picture. We make the (questionable) assumption that the perturbation parameters $\delta\alpha(CH_3)$, $\delta\alpha$(*t*-butyl), $\delta\alpha$(trim.-silyl), are the same as those derived above for the π-orbital energies. Furthermore we postulate that the lone-pair orbital $11\mathbf{a}_1(\sigma)$ can be approximated by a zero-differential overlap linear combination

$\psi_n \approx \Sigma_\mu C_{n\mu} \chi_\mu$ of local hybrid orbitals χ_μ and that the contributions of an electron moving in $11a_1(\sigma)$ to the individual atomic charge populations Q_μ are $C^2_{n\mu}$, with $\Sigma_\mu C^2_{n\mu} = 1$.

Substitution in position ξ by a group R leads to a shift

$$\delta\varepsilon(\psi_n) = \frac{1}{3}(3\,C^2_{n\xi} + C^2_{n\tau} + C^2_{n\tau'}) \cdot \delta\alpha(R) = a_n\,\delta\alpha(R) \qquad (11)$$

if $\varkappa(R) = 0$ and $m = 1/3$ see (5) and (7)). As before, τ and τ' are the positions *ortho* to ξ. From the data given in Table 6 and with $\delta\alpha(CH_3) = 1.2$ eV, $\delta\alpha(t\text{-butyl}) = 1.5$ eV and $\delta\alpha$(trim.-silyl) = 2.4 eV, we find that a_n does not depend significantly on ξ, *i.e.* that $a_n = 0.16 \pm 0.05$ for all positions $\xi = 2$ to 6.

The definition of a_n given in (11) together with $a_n = $ const. and $\Sigma_\mu C^2_{n\mu} = 1$ leads to four linear equations in the unknowns $C^2_{n\mu}(\mu = 1,2,3,4)$. Under the limiting condition $C^2_{n\mu} > 0$, the solution with minimal value of a_n is $C^2_{n,1} = 0.50$, $C^2_{n,2} = C^2_{n,6} = 0{,}000$, $C^2_{n,3} = C^2_{n,5} = 0.20$, and $C^2_{n,4} = 0.10$. We find $a_n = 0.23$, in reasonably good agreement with the mean experimental value. (All other solutions compatible with the above conditions yield $a_n > 0.23$). The delocalization of the lone-pair electrons over the σ-system implied by the coefficients $C^2_{n\mu}$ is roughly similar to that derived from molecular orbital models of pyridine [11].

For our interpretation of the PE. spectra (see Fig. 2,3 and 4) the top occupied molecular orbital in the parent compound pyridine (I) is taken to be the 'lone pair' orbital $11a_1(\sigma)$. The corresponding band (9.6 eV) overlaps strongly with the first π-band ($1a_2(\pi)$, 9.7_5 eV). This assignment is also proposed by *Brundle, Robin, Kuebler & Basch* and by *Lindholm et al.* [6].

Finally we compare our perturbation parameters $\delta\alpha$(trim.-silyl) and $\varkappa^2$(trim.-silyl)/$(\varepsilon(\psi_J) - \varepsilon(\phi_\rho))$ with those derived by *Bock et al.* [3] [4] [15] [16] [17], from the ionization potentials of a large series of trimethylsilyl-substituted compounds (*KRUPP MAT CH4* mass spectrometer; *Fox* ion source):

a) From trimethylsilyl-substituted ethylenes: $\delta\alpha$(trim.-silyl) = 2.4 eV; $\varkappa^2$(trim.-silyl)/$(\varepsilon(\psi_J) - \varepsilon(\phi_\rho)) = -1.6$ eV.

b) From trimethylsilyl-substituted benzenes: $\delta\alpha$(trim.-sily) = 2.6 eV; $\varkappa^2$(trim.-silyl)/$(\varepsilon(\psi_J) - \varepsilon(\phi_\rho)) = -1.7$ eV.

These values are in excellent agreement with ours. However, the destabilization of 0.84 eV of the carbonyl 'lone pair' orbital, on going from *t*-butyl-phenyl ketone to trimethylsilyl-phenyl ketone, is much larger than would be expected from a simple HMO model for benzaldehyde.

The ESR. spectra of radical anions of trimethylsilyl-substituted hydrocarbons have been interpreted by *Gerson, Heinzer & Bock* [19] in terms of a simple HMO model with $\alpha_{Si} = \alpha - 1.5\beta$ and $\beta_{SiC} = 0.55\beta$, neglecting inductive perturbations due to the trimethylsilyl substituents. This model would lead to an increase rather than to the observed decrease in ionization potential on trimethylsilyl substitution. A much larger β_{SiC}-value would be required to account for the $Si \leftarrow \pi$ back-donation effect described by $\varkappa^2$(trim.-silyl)/$(\varepsilon(\psi_J) - \varepsilon(\phi_\rho)) = -1.5$ eV. But, since the model in question was put forward to explain the behaviour of the lowest antibonding molecular orbital of pyridine under the influence of trimethylsilyl substituents, it can hardly be expected to describe ionization phenomena very well.

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Experimental. – The samples of 2-trimethylsilyl-pyridine (VI) and 4-trimethylsilyl-pyridine (VII) were prepared according to the procedures outlined by *Anderson, Bradney & Webster* [20].

2,6-Bis-(trimethylsilyl)-pyridine (IX). To a solution of *n*-butyllithium (110 ml; 2.25 M) in 250 ml of anhydrous ether cooled to $-75°$ and under an anhydrous nitrogen atmosphere was added 2,6-dibromopyridine (23.7 g; 0.1 mole) as a solid *via* a dry funnel. After stirring for 1 hour at $-75°$, trimethylchorosilane (27 g.; 0.25 mole) was added dropwise over a 10 minute period. The mixture was then allowed to warm to room temperature and was stirred for an additional 7 h. After filtration of the lithium chloride, the solution was concentrated *in vacuo* and fractionally distilled to afford 20 g (89.5%) of IX, b.p. 123°/25 Torr, $n_D^{25} = 1.4740$. NMR: 7.31 δ (*S*, 1H, pyridyl), 0.29 δ (*S*, 6H, $SiMe_3$). Elemental analysis see below.

2.5-Bis-(trimethylsilyl)-pyridine (VIII). The reaction of *n*-butyllithium (100 ml.; 2 M), 2,5-dibromopyridine (20 g; 0.2 moles) and trimethyl-chlorosilane (21.7 g; 0.2 moles), according to the procedure for the preparation of IX, afforded after recrystallization from heptane of the resultant solid product 13 g (69.2%) of VIII, m.p. 82–84° NMR: 8.82 δ (distorted *S*, 1H, $H_{(6)}$), 7.60 δ (distorted *d*, 1H, $H_{(4)}$), 7.35 δ (distorted *d*, 1H, $H_{(3)}$), 0.27 δ (split *S*, 18H, 2-SiMe and 5-$SiMe_3$).

$C_{11}H_{21}NSi_2$ Calc. C 54.11 H 9.49 Si 25.14 IX: Found C 58.98 H 9.51 Si 25.40%
VIII: " " 59.01 " 9.64

PE. Spectra: recorded on a modified PS-15 photoelectron spectrometer of *Perkin-Elmer Ltd.* (Beaconsfield, England) of the type described by *Turner* [21]. For experimental details see [22].

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32. Notiz über die Photoelektronen-Spektren des Nortricyclens und des Triasterans[1])

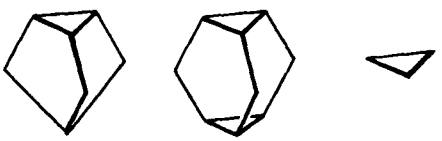
von **E. Haselbach, E. Heilbronner, H. Musso** und **A. Schmelzer**

Physikalisch-Chemisches Institut der Universität Basel
und
Institut für Organische Chemie der Universität Karlsruhe

(11. XI. 71)

Summary. The photoelectron spectra of nortricyclene (= tricyclo[2.2.1.$0^{2,6}$]heptane) and of triasterane (= tetracyclo[3.3.1.$0^{2,8}$.$0^{4,6}$]nonane) have been recorded and a tentative assignment of the bands has been put forward on the basis of MINDO/2 SCF calculations.

In Fig. 1 sind die Photoelektronen-Spektren (= PE.-Spektren) des Nortricyclens I (= Tricyclo[2.2.1.$0^{2,6}$]heptan) und des Triasterans II (= Tetracyclo[3.3.1.$0^{2,8}$.$0^{4,6}$] nonan) abgebildet. Beide Kohlenwasserstoffe enthalten den Cyclopropanring als charakteristische Einheit.



I(C_{3v}) II(D_{3h}) III(D_{3h})

Basch, Robin, Kuebler, Baker & Turner [2] konnten anhand des PE.-Spektrums von Cyclopropan III zeigen, dass die ersten drei Banden den folgenden Orbitalen zuzuordnen sind: Bande ①: *Walsh*-Orbital $3\mathbf{e}'$(CC) [3], ε_{exp} ($3\mathbf{e}'$) = −10,9 eV (*Jahn-Teller*-Aufspaltung 0,8 eV, vgl. [4]); Bande ②: Orbital $1\mathbf{e}''$(CH), ε_{exp} ($1\mathbf{e}''$) = −13,2 eV (*Jahn-Teller*-Aufspaltung $< \sim 0{,}3$ eV, vgl. [4]); Bande ③: *Walsh*-Orbital $3\mathbf{a}_1'$(CC), $\varepsilon_{exp}(3\mathbf{a}_1') = -15{,}7$ eV. Bei der Zuordnung «experimenteller» Orbitalenergien $\varepsilon_{exp}(\psi)$ haben wir implizit vom *Koopmans*-Theorem in der Form $\varepsilon_{exp}(\psi_J) = -I_{v,J}$ Gebrauch gemacht, wobei $I_{v,J}$ das vertikale Ionisationspotential derjenigen Bande Ⓙ ist, die mit dem Orbital ψ_J korreliert wurde.

[1]) 32. Mitteilung über «Anwendungen der Photoelektronen-Spektroskopie». 31. Mitteilung: [1].