Ionisation Energies of Pyridine N-Oxides determined by Photoelectron Spectroscopy

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High resolution HeI photoelectron spectra of twelve pyridine *N*-oxides are presented. The exceptional separation of the first four, or more, bands throughout the series allows assignments of these in relation to the proposed scheme for pyridine *N*-oxide. These are discussed in view of the vibrational detail discernible, variations in the relative intensities of the bands with HeII and HeI radiation, especially in the chloro derivatives, and substitution trends. The correlation of the assignments alfords a probe for substituent effects on the ground and first two excited states from the well defined changes in the corresponding ionisation energies. The latter are considered in terms of dipole perturbations due to the substituents. The linear regressions observed for the *para*-substituted derivatives between the first three ionisation energies and dipole moments, basicities and reactivity constants are discussed.

Heterocyclic *N*-oxides have aroused much chemical interest with the realisation of their importance as synthetic reagents, catalysts, ligands and the biological activity associated with some of the naturally occurring species.¹ These have instigated many studies in the photochemical field,² for example, and have been subject to a broad spectrum of physico-chemical measurements.¹ U.v. spectroscopy in particular has been prominent.³ Most studies have been on the neutral molecules though the anion



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radicals were examined by u.v., e.s.r. and polarography,⁴ and some cation radicals by e.s.r.⁵

We have embarked on the study of the electronic structure of the N-oxides of azaaromatic compounds by high resolution photoelectron (p.e.) spectroscopy. In this contribution we consider the p.e. spectra of the pyridine N-oxides (1)-(12).

In contrast to the p.e. spectra of most aromatic systems where the conglomeration of bands particularly with substituents usually limits the assignment,⁶ the p.e. spectra of the pyridine N-oxides show a clear separation of the first four (or more) bands. This affords a probe for the effect of substituents on the ground (\tilde{X}) , first excited (\tilde{A}) and two higher excited ionic states, associated with the ionisation of electrons of the oxygen "lone-pairs" of π and σ symmetry and of the ring π -orbitals respectively.

EXPERIMENTAL

The p.e. spectra were recorded on a spectrometer based on the design of Turner.⁷ The analyser is a 10 cm radius $\pi/\sqrt{2}$ cylindrical condenser and the source of excitation is a d.c. capillary discharge with conditions adjusted for output of $HeI\alpha(21.22 \text{ eV})$ or $HeII\alpha(40.80 \text{ eV})$ radiation.

The HeI spectra were all recorded with high resolution, 0.02 eV or better, full width at half-height for 5 eV electrons. When HeII radiation was used some resolution was sacrificed in favour of flux. The ionisation energy (i.e.) scale was calibrated in situ with the rare gases, with naphthalene and with the photoelectrons obtained by the ionisation of xenon by the HeI β (23.09 eV) radiation.

The samples were either commercial products (1), (2), (3), (4), (7), (8), (10) or were prepared from the corresponding substituted pyridines by oxidation with hydrogen peroxide as described in the literature (5), (9).⁸ [${}^{2}H_{5}$]Pyridine *N*-oxide was prepared from [${}^{2}H_{5}$]pyridine by oxidation with 30 % D₂O₂ (in D₂O) and deuteroacetic acid. The product [²H₅]-(1) was extracted from the aqueous phase while any remaining $[{}^{2}H_{5}]$ pyridine was contained in the dichloromethane phase. Compound (6) was prepared from (5) by the method described except that pure liquefied dimethylamine was employed. Attempted synthesis of (11) (2-CN) by oxidation of 2-cyanopyridine under the conditions prescribed,¹⁰ consistently resulted in 2-carboxy pyridine N-oxide. Compound (11) was prepared however from 2-cyanopyridine (1.2 cm³) when oxidised with 90 % hydrogen peroxide (1.5 cm³) in glacial acetic acid (3.6 cm^3) at 70°C for 45 min. After extraction and two vacuum sublimations \approx 0.9 g of (11) was acquired, m.p. = 120°C in accord with that given in ref. (10). Pentachloropyridine N-oxide (12) was kindly provided by Prof. H. Suschitzky.¹¹ All the samples were purified prior to use and checked for chemical purity.

In the p.e. spectra of the N-oxides studied at the lower temperatures ($\approx 20-100^{\circ}$ C) some variation was noted in the relative intensities of the two most intense vibrational components as well as the breadth of the second component in the first two bands (cf. fig. 3). However, no shift in the i.e. of their maxima was detected. For compound (1) the i.e. values quoted were reproduced on three different $\pi/\sqrt{2}$ p.e. spectrometers. In view of the extreme hygroscopic nature of the N-oxides these variations may well be associated with sample pressure fluctuations. On the low i.e. tail of the first three bands there is evidence of vibrational hot bands (fig. 3).

RESULTS

The HeI p.e. spectra are shown in fig. 1-2a. The bands below i.e. \sim 13 eV are exceptionally well separated. It will be shown that in compound (1) these 4 bands are attributable to π and σ p-type orbitals localised essentially on the oxygen and to the ring π -orbitals related to the e_{1g} pair in benzene.⁶ When substituents are introduced, additional band(s) may be seen in this region due to the π -orbitals of the substituent (X), $X = N(CH_3)_2$, OCH₃ or σ -lone-pairs, X = CN, or both, as is the case for X =Cl, NO₂. Nevertheless, the bands are always sufficiently distinct to permit clearcut



FIG. 1.—HeI photoelectron spectra of the pyridine N-oxides (a) (1), (5), (12) and pentachloropyridine and (b) the pyridine N-oxides (2), (8), (9) and (3).

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FIG. 2.—(a) HeI photoelectron spectra of the pyridine N-oxides (7), (4) and (6) and (b) He II photoelectron spectra of compounds (1), (5), (12) and pentachloropyridine.

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FIG. 3.—Expansion of the first three bands in the HeI photoelectron spectra of compounds (1), $[{}^{2}H_{s}]$ -(1), (5) and (3).

assignments. In table 1 are presented the experimental vertical i.e. values and the propounded assignments are summarised. For convenience C_{2v} symmetry representations are used in part for the molecules with the coordinate system as shown in fig. 4. The listed vertical i.e. values are ± 0.02 eV when the vibrational fine structure is distinct or ± 0.05 eV for the maxima of the broader bands.

In fig. 2(b) are reproduced the HeII p.e. spectra of compounds (1), (5), (12) and of pentachloropyridine. Also shown is the HeI spectrum of the latter [fig. 1(a)] for comparison. Although the HeI spectrum has been published ¹² no i.e. values were given; the present spectrum is well-resolved.

Vibrational fine structure is abundant under high resolution conditions on the first three bands (fig. 1, 2) and in fig. 3 are shown the expanded sections of these in the p.e. spectra of compounds (1), $[{}^{2}H_{5}]$ -(1), (5) and (3) as examples. The suggested analyses

TABLE 1.—IONISATION ENERGIES (eV	/) OF	THE PYRIDINE .	N-OXIDES	(1))-(12)
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compound	$I_1 a(\pi O:)$	$I_2(\sigma O:)$	$I_3(\pi a_2)$	14	<i>I</i> ₅	I_6
(1)	8.38	9.22	10.18	11.59 (<i>πb</i> 1)	$13.0 (\pi b_1)$	13.8
(2) (4-CH ₃)	8.12	9.02	10.07	$11.18 (\pi b_1)$	12.5	13.3
(3) (4-CN)	8.95	9.74	10.84	$11.58 (\pi b_1)$	12.18 º (σN ;)	13.0
(4) (4-OCH ₃)	7.74	8.78	9.97	10.50	12.08	13.7
(5) (4-Cl)	8.42	9.31	10.44	11.14	11.87	13.5
$(6) (4-N(CH_3)_2)$	7.21	8.65	$9.03 (\pi b_1)$	9.92 (πa_2)	$11.62 (\pi b_1)$	12.5
(7) (4-NO ₂)	9.03	9.80	10.81	11.26	11.46	12.3
(8) (3-CH ₃), [(10) (2-CH ₃)]	8.20 [8.21]	9.02 [8.99]	9.80 [9.79]	11.20[11.39]	12.60	13.35
(9) (3-CN), [(11) (2-CN)]	8.93 [8.96]	9.68 [9.76]	10.56 [10.49]	11.90	12.50 b (oN :)	13.18
(12) (-Cl ₅) c	8.72	9.60	10.87	11.52	12.0	13.4

The numbering of the bands *i* in fig. 1, 2 corresponds to the index *i* of the ionisation energies I_{t} . *a* For nomenclature of assignment see text; *b* vibrational spacing 1850 cm^{-1} , *c* i.e. values of pentachloropyridine: $I_1-9.44, I_2-10.28, I_3-10.60, I_4-11.38, I_5-11.65 \text{ eV}$; *a* i.e. value of trimethylamine *N*-oxide: $I_1-8.25, I_2-12.6 \text{ eV}$.

for the discernible progressions are indicated. In table 2 are given the corresponding ionic frequencies. It must also be pointed out that the vibrational analyses proposed (fig. 3) for the third bands are more tentative. We have also studied the p.e. spectrum of compound $[{}^{2}H_{5}]$ -(1) to compare with that of (1). As can be seen in fig. 3, there are no clear changes in the vibrational pattern and any CH mass dependence is not

TABLE 2.—VIBRATIONAL FREQUENCIES (WAVENUMBER/cm⁻¹) EXCITED IN THE GROUND (\tilde{X}) , FIRST (\widetilde{A}) and second (\widetilde{B}) ionic states of the pyridine N-oxides

pyridine N-oxide	$\mathbf{\widetilde{x}}$	Ã	B
(1)	520	1250, 810, 520	480
$[^{2}H_{5}]$ -(1)	520	1250, 810, 520	1450, 520, 280
$(2), (8), (10) (X = CH_3)$	480	1210, 810, 360	
(3), (9), (11) (X=CN)	400	1210, 810, 400	1210, 500, 280
(4) (4-OCH ₃)		1290	1290
(5) (4-Cl)	400	1210, 810, 360	1370, 320
$(7) (4-NO_2)$	400	1210, 810, 320	
$(12) (-Cl_5)$	520		1210

perceptible within these experimental limits. Then if we consider only the 11 totally symmetric fundamentals (in $C_{2\nu}$) of compound (1), as is probably reasonable in view of the Franck-Condon factors, it is possible to attribute the most prominent vibrational progression, 1250 cm⁻¹, on the second band to the N-O stretching frequency while the 520 cm⁻¹ frequency, discernible on the bands, is allotted to a ring vibration.¹³ The ground molecular state frequencies are 1243 and 544 cm⁻¹ respectively.¹³

It is notable that substitution in most instances does not markedly affect the vibrational features observed in compound (1) and this fits well with the assignments.

DISCUSSION

We first assign the bands in the p.e. spectrum of compound (1) which correspond to the ionisation processes leaving the radical cation in the ionic states \hat{X} , \hat{A} , \hat{B} etc. The photoelectrons generating these bands can be considered as originating from the respective molecular orbitals (MOs) by means of which the closed-shell parent species is described.14

Pyridine N-oxide (1), may be considered as a monosubstituted benzene where the

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N-O replaces the C-H group. Consequently the degeneracies of the MOs are removed by interaction with the MOs of the N-O group. In the p.e. spectra of $(CH_3)_3NO$ (i.e. values in footnote d to table 1) and CF_3NO^{15} the first ionisation process (i.e. values of 8.25 and 10.40 eV respectively) relate to the degenerate oxygen lone-pairs while the subsequent i.e. in $(CH_3)_3$ NO is ≈ 12.6 eV. Thus we anticipate that two additional bands to the two in the p.e. spectrum of benzene ⁶ (i.e. = 9.25 eV) will be present in the low i.e. region in the p.e. spectrum of compound (1). Indeed, four bands are observed [fig. 1(a) (1)-(4)] below i.e. $\approx 12 \text{ eV}$. From comparison of the i.e. data of the lone-pairs in alcohols, ketones ¹⁶ and halogenoacetylenes ¹⁷ with $(CH_3)_3$ or CF₃, and CH₃ groups in the β position the first i.e. values of $(CH_3)_3$ NO and CF₃NO both give the oxygen lone-pair basis in the $9-9\frac{1}{2}$ eV range for the environment in compound (1). Then the second band 2 in the spectrum of (1) [fig. 1(a)] can be associated with the oxygen σ -lone-pair, $\sigma 0$: (b_2) (cf. fig. 4). By comparison, the mean of the i.e. values leading to singlet and triplet states on ejection of photoelectrons of the oxygen lone-pair in nitroxide radicals is also $\approx 9 \text{ eV}$.¹⁸ The dominant vibrational progression observed on the second band O (fig. 3) and attributed to the N—O stretching vibration is also then reasonable.



FIG. 4.—Qualitative representation of the five MOs of pyridine N-oxide associated with the first five bands in the p.e. spectrum [fig. 1(a)]. The coefficients shown were calculated by the MINDO/2 procedure.

The assignment of the other three bands in this region (1, 3, 4) follows directly. The symmetric (w.r.t. xz plane fig. 4) πb_1 -orbital of the benzene e_{1g} pair is stabilized in preference to the antisymmetric component, πa_2 , as the latter has a nodal plane at the point of substitution. The oxygen p_x -lone-pair can only interact with the symmetric component and thus the first band (1) is associated with the out-of-phase combination $(\pi 3b_1)$, while the fourth band ④ with the in-phase $(\pi 2b_1)$ and band ③ with the πa_2 These are depicted qualitatively in fig. 4.* The lowest π -MO in compound (1) MO. $(a_{2u} \text{ in benzene})$ is also of b_1 symmetry but lies much deeper $\approx 13 \text{ eV}$. Furthermore, the composition of the MO connected with the first ionisation process is heavily biased in favour of the oxygen p_x basis. The coefficients of the oxygen, p_x and p_y , orbitals in the two highest occupied MOs are calculated by MINDO/2 or CNDO/2 as 0.7 and 0.86 respectively. Thus we may refer to these as oxygen π and σ lone-pairs (fig. 4). The highest occupied MO characteristics have also been predicted previously by calculations, e.s.r. studies of the radicals, and electronic spectra to be of π -type with a predominating contribution from the oxygen $p_x \text{ AO}^{3-5}$ A more detailed discussion

^{*} In fig. 4 are also shown the coefficients of the eigenfunctions as calculated by MINDO/2. The CNDO/2 values are very similar.

of the p.e. spectroscopic data of compound (1) in relation to these studies is more appropriate in conjunction with the p.e. spectra of the *N*-oxides of the azabenzenes.¹⁹ We also note here that an empirical linear correlation between the i.e. of the πa_2 in monosubstituted benzenes (ϕX) and their experimental dipole moments (μ) exists :

i.e.
$$\pi a_2(\phi X) = 0.19\mu + 9.35$$

(correlation coefficient r = 0.946, degrees of freedom n = 14). From the dipole moment of compound (1), 4.130 D,²⁰ the predicted i.e. of the πa_2 MO is then 10.13 eV, supporting our assignment of band (3), i.e. = 10.18 eV. This also suggests that the inductive stabilisation of the N—O group is comparable to the cyano group, for example. The proposed assignment for compound (1) is further supported by the trends on substitution and the HeII p.e. spectra of (1), (5) and (12) [fig. 2(b)].

Fluorination is a useful procedure for distinguishing π and σ bands in the p.e. spectra as the σ states are appreciably more stabilized than the π .¹⁶ However, substitution by chlorine can provide an alternative when HeII radiation is available. The decrease in ionisation cross-section of the chlorine 3*p* AO in passing from 58.4 to 30.4 nm wavelength of incident radiation is greater than that of 2*p* AOs.²¹ This suffices for the effect to be discernible in the HeI and HeII p.e. spectra of molecular systems and the relative changes in intensity of the bands are, *qualitatively*, a reflection of the contribution of the Cl 3*p* AO(*s*) basis in the MO in question.

The HeII p.e. spectra of the chlorine containing species [fig. 2(b)] show considerdifferences from the HeI spectra (fig. 1) in the relative intensity of the bands.* The most drastic changes occur for the bands in the 12-13 eV energy region. These bands are associated with the MOs predominantly of chlorine character, chlorine "lonepairs".

In the HeI and HeII spectra of compound (1) comparatively small changes are seen in the relative intensities of the first four bands, while in the spectra of (5) changes are already apparent. Bands ①, ④ and ⑦ decrease in intensity in relation to bands ② and ③. This is in accord with the assignment for compound (1) as the πb_1 MOs associated with these bands mix with the chlorine $3p_x$ AO in (5). In addition, in the HeII spectra of compounds (1) and (5), intensities of bands ② (w.r.t. ③) are enhanced somewhat in agreement with O2p/C2p ionisation cross-section variation for MOs of O2p and C2p composition respectively.²²

In the HeII spectrum of pentachloropyridine [fig. 2(b)] the first band is depressed in intensity relative to bands (2) and (3). This agrees with the published assignment ¹² to the πa_2 MO which has a larger chlorine 3p char acter than the $\pi 2b_1$ MO (band (2) or (3)). In the HeII spectrum of compound (12) the intensity drop of band (3) suggests that the sequence of MOs of (1) for the first three bands still holds. Band (4) (and possibly (7)) may also be correlated with the $\pi 2b_1$ (and πb_1) MOs of compound (1) in view of the HeII/HeI intensity variation. This would indicate that the three i.e. values of compound (12) have increased in respect to those of (1). For the first two bands, this stabilisation is reasonable due to the dominant dipole influence, as the electron density is largely concentrated around the oxygen. This is already apparent in the increase of the first three i.e. values of compound (5) with respect to those of (1). However, the large influence on the πa_2 MO in compound (12) is anomalous, as conjugative interaction should be considerable in comparison to chlorobenzenes.^{6, 28} The alternative interpretation is then to reverse the assignments of bands (2) and (3), notwithstanding the intensity changes and a surprising magnitude of the stabilisation

* The increase in intensity of bands above i.e. \approx 15 eV is, to a large extent, due to the discrimination of the analyser against slow photoelectrons when HeI radiation is used.

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 $(\approx 1.6 \text{ eV})$ of the $\sigma 0$: band. However, the Franck-Condon profile of the band (3) of compound (12) does resemble band (2) of (1).

SUBSTITUENT CONSEQUENCES

In the p.e. spectra of the pyridine N-oxides (2)-(12) the separation of the first group of bands remains. Additional bands, in the region of the first four bands (<13 eV) in the p.e. spectrum of compound (1) are readily identified by comparison to the p.e. spectra of substituted benzenes.²³ In the *para*-derivatives the consequences of the nodal differences of the b_1 and a_2 π -MOs are again evident. Thus in compounds (4) and (6) [fig. 2(*a*)] the additional band is due to the low i.e. of the basis of the lone-pair electrons of oxygen and nitrogen 10.2 eV and 8.7 eV respectively,²⁴ which mix considerably with the πb_1 MOs. Bands (4) and (5) in the spectrum of compounds (4) and (6) respectively are ascribed to MOs which have the largest contribution from these lone-pairs, in compound (7) the bands (4) and (5) [fig. (2*a*)] can be attributed to the MOs characteristic of the nitro group while in compounds (3), (9), (11) bands (5) are those of the nitrogen, lone-pair of the cyano group.⁶ The p.e. spectra of the chlorine containing species (5) and (12) have been described previously. In the substituted pyridine N-oxides the bands can be allotted to MOs within the model for compound (1) (fig. 4), as is summarised in table 1.



FIG. 5.—Correlation between the p.e. spectroscopic i.e. values and the MINDO/2 i.e. values for the π -bands, and in the insert of the oxygen sigma lone-pair bands, of the pyridine N-oxides.

The p.e. spectra of the two *meta*-derivatives (8) and (9) suffice to confirm the assignment. The i.e. values of bands (1) and (2) in compounds (2) and (8), or (3) and (9), barely differ in contrast to bands (3) (table 1). The latter however lie ≈ 0.2 -0.3 eV to lower i.e. for the *meta*-compounds. This destabilisation shows the contribution of through-space overlap of the deeper-lying π -MOs of the substituent with the π -MO of the ring [πa_2 in compound (1)] absent in the *para*-species. For *ortho*-derivatives (10) and (11), the p.e. spectra show a great deal of similarity to those of the corresponding *meta*-compounds. In the higher i.e. region there are some slight differences. These trends are also observed in disubstituted benzenes.²⁵

For most of the molecules studied, we have carried out semi-empirical SCF calculations to compare the eigenvalues with the i.e. values observed. The relative

order of the π -levels were best represented by the MINDO/2 procedure.* In all cases the π -MO sequences suggested (table 1) are in accord with the calculations. In fig. 5 is shown a least-squares linear correlation between the p.e. spectroscopic i.e. values (<12 eV) and the MINDO/2 i.e. values (Koopmans' values) for the π -MOs. The insert shows the $\sigma 0$: correlation. In table 3 are given the analysis of the regressions (1) and (2). Extrapolating of regression (1) yields an i.e. $\sim 13 \text{ eV}$ for the deepest π -band of compound (1) (fig. 1 band (5)) from the calculated MINDO/2 value.

TABLE 3.—COMPILATION OF THE REGRESSIONS $I_i = aX + b$, subjected to a least-squares ANALYSIS AND DISCUSSED IN THE TEXT. I_i are the i.e. values of the para-substituted PYRIDINE N-OXIDES

Ii	X	a	b	correlation coefficient (r)	degrees of freedom (n)	relation number
$I_i(\pi)^a$	i.e.(MINDO/2)	1.03 ± 0.04	-0.98 ± 0.39	0.987	21	(1)
$I_2(\sigma 0:)$	i.e.(MINDO/2)	0.90 ± 0.15	0.30 ± 1.50	0.935	5	(2)
$I_1(\pi 0:)$	μ	-0.29 ± 0.03	9.31 ± 0.14	-0.968	5	(3)
$I_2(\sigma 0:)$	μ	-0.20 ± 0.02	9.94 <u>+</u> 0.07	-0.980	5	(4)
$I_3(\pi a_2)$	μ	-0.17 ± 0.02	10.95 ± 0.07	-0.974	5	(5)
$I_1(\pi 0:)$	pK _a	-0.33 ± 0.02	8.51 ± 0.04	-0.992	4 c	(6)
$I_2(\sigma 0:)$	pK_a	-0.22 ± 0.03	9.37 ± 0.05	-0.974	4	(7)
$I_3(\pi a_2)$	pK_a	-0.17 ± 0.03	10.42 ± 0.07	-0.929	4	(8)
$I_1(\pi 0:)$	$\sigma(\mathbf{X})$	1.15 ± 0.09	8.20 ± 0.05	0.985	5	(9)
$I_{1}(\pi 0:)$	$\sigma^+(X)$	0.75 ± 0.03	8.40 ± 0.03	0.995	5	(10)
$I_2(\sigma 0:)$	$\sigma(X)$	0.78 ± 0.08	9.18±0.04	0.974	5	(11)
$I_2(\sigma 0:)$	$\sigma^+(\mathrm{X})$	0.49±0.07	9.22 ± 0.06	0.949	5	(12)
$I_{3}(\pi a_{2})^{b}$	$\sigma(\mathbf{X})$	0.66 ± 0.10	10.28 ± 0.05	0.946	5	(13)
$I_{3}(\pi a_{2})^{b}$	$\sigma^+(\mathrm{X})$	0.40 ± 0.09	10.39 ± 0.07	0.891	5	(14)
$I_1(\pi 0:)$	$I_2(\sigma 0:)$	1.43 ± 0.14	-4.90 ± 1.26	0.978	5	(15)
$I_1(\pi 0:)$	$I_3(\pi a_2)$	1.55 ± 0.29	-7.69 ± 2.99	0.922	5	(16)
$I_2(\sigma 0:)$	$I_3(\pi a_2)$	1.12 ± 0.11	-2.35 ± 1.15	0.976	5	(17)

^{*a*} π -i.e. values below \approx 12 eV; excludes compound (3) (lack of convergence of MINDO/2) and compound (5); ^b in compound (6) read $I_4(\pi a_2)$; ^c pK_a values of compound (3) not found.

In table 4 are shown the changes of i.e. of the σO : and πa_2 bands in *para*-substituted pyridine N-oxides and included are the changes observed in the i.e. of the πa_2 bands in the corresponding benzenes. The magnitude of the changes of the σO : bands [cf. i.e. (πa_2)] are somewhat surprising for substituents as far removed. With electron

TABLE 4.—DIFFERENCES BETWEEN THE I.E. VALUES OF $\sigma 0$: AND OF πa_2 bands in *para*-substi-TUTED PYRIDINE N-OXIDES TO THESE I.E. VALUES IN PYRIDINE N-OXIDE AND THE DIFFERENCE IN THE I.E. VALUES OF πa_2 bands of monosubstituted benzenes to that in benzene

_	pyridine	1	
х	$\Delta i.e. (\sigma 0 :)/eV$	$\Delta i.e. (\pi a_2)/eV$	$\Delta i.e. (\pi a_2)/eV$
NO_2	0.58	0.63	1.10
CN	0.52	0.66	0.90
Cl	0.09	0.26	0.44
CH ₃	-0.20	-0.11	-0.25
OCH ₃	-0.44	-0.21	-0.04
$N(CH_3)_2$	-0.61	-0.35	-0.25

* Standard geometry and N-O bond length of 1.26 Å (MINDO/2 and CNDO/2 minimum energy value) were used. The coplanar conformation was predicted but the potential minimum was shallow for deviation up to $\approx 20^{\circ}$ above, or below, the ring plane of the O atom.

donating substituents especially, a more pronounced destabilisation of the σO : MOs than the πa_2 MOs is evident. The smaller changes of the πa_2 bands of the *N*-oxides with electron withdrawing substituents than are observed with the corresponding benzene are perhaps a consequence of dipole-dipole interactions between the substituent and the N—O group.[†]

The inductive effects of substituents have been interpreted by a short range and a long range term ²⁶ which can be represented through a change in a Coulomb integral of the adjacent atom, and the interaction of the dipole of the substituent with the remaining atoms not attached respectively. It was found that the i.e. values associated with the π O:, σ O: and πa_2 MOs give a good linear regression with the dipole moments of the molecules.²⁷ For the sake of conciseness the details of relations (3), (4), (5) and other linear relations (least squares analyses) obtained are collected in table 3 and in fig. 6(*a*) are shown the regressions. If one represents the long-range inductive term by ²⁶

$$\sum_{i \neq j} \binom{e}{\varepsilon} \frac{\mu \cdot r_i}{r_i^3} c_i^2$$

. .

where ε is the dielectric constant of the framework, r_i is the vector position of atom *i* with respect to the point dipole of the group attached at position *j*, then by expansion of this term about a common point of origin (*r*) for all the substituents, a linear regression of the form observed [relations (3)-(5) table 3] is obtained from the first term of the expansion. With monosubstituted benzenes and *para*-substituted pyridine *N*-oxides the slopes of the i.e.(πa_2) against dipole regressions are 0.19 (given earlier) and 0.18 [table 3 relation (5)] respectively.

For a distance of ≈ 1.4 Å, from the atom of the ring where the substituents are attached, as the common point, the observed slopes yield dielectric constants $\varepsilon \approx 1.6$ and ≈ 1.4 respectively for the sigma electron framework. In halogenobenzenes the values $\varepsilon = 2.28^{28}$ and $\varepsilon = 2.95^{26}$ were obtained, where the centre of the C-X bond was taken for the origin. The dependence of the first two i.e. values on the dipole moments is in accord with the concentration of the electron density around the oxygen in the two MOs and with the small electron density at the point of the para-substituent. The short-range inductive term and the destabilisation as consequence of overlap are not so important. The latter terms are, however, significant in benzenes and a linear dependence of the first i.e. on the dipole moments is not obtained. We also note that the slopes of the regressions (3), (4) (table 3) differ. Furthermore, with the approximations made, the perturbation of the oxygen (σO :) i.e. values is estimated to be nearly the same for *para* and *meta* substituents, whereas a factor of two or so larger with ortho. Indeed the σO : i.e. values of compounds (2) and (8), and (3) and (9) are very similar, but so are those of compounds (10) and (11) respectively. Nevertheless, this is reasonable as in compound (4) the proximity of the substituents may result in the destabilisation of the σO : MO by interaction with the deeper lying π -MOs of the cyano group, while the anticipated changes in compound (10) are small.

The first two i.e. values also yield good regressions [relations (6), (7)] with the pK_a values,²⁹ as does the i.e. (πa_2) (8); though it is not as good. This is reasonable since protonation occurs at the oxygen. In addition, these three i.e. values correlate very well with σ [fig. 6(b)] and σ^+ reactivity constants,³⁰ relations (9)-(14). It could be argued that the πO : i.e. correlates better with σ^+ whereas σO : i.e. and πa_2 i.e. with σ , in harmony with the differences in the derivation of the σ and σ^+ values. The analogy between pyridine N-oxide and the phenoxide anion is evident. It is worth noting that

[†] For the electron donating substituents, the differences are not so significant as the i.e. values of the πa_2 bands in the benzenes are not well defined.



FIG. 6.—Correlation between the first three i.e. values of the pyridine *N*-oxides and (*a*) dipole moments, (*b*) reactivity constants.

the significantly greater gradient of relations (9) [or (10)] than of (11), (13) [or (12), (14)] suggests a more pronounced influence of the substituents on the ground ionic state than on the excited ionic states. This is also shown independently on the reactivity indices, by the internal relationships between these three i.e. values, relations (15)-(17). In contrast the i.e. values of the bands correlated with the $\pi(2b_1)$ in compound (1) do not yield significant linear correlation with any of the parameters mentioned above.

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These correlations of the i.e. values with other experimental entities confirm that the pyridine N-oxides provide an exceptional model for the study of substituent effects on the i.e. values of an aromatic system. Hitherto, such extensive p.e. data were available only for substituted benzenes.^{6, 23} However, in the p.e. spectra of pyridine N-oxides the changes are accurately discernible and available also for the first two (or more) excited ionic states of known characteristics in the whole series.

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NOTE ADDED IN PROOF

A communication by the authors on the assignment of the p.e. spectra of the pyridine *N*-oxides has been published. *Tetrahedron Letters*, 1974, 2987, instigated by a paper (M. A. Weiner and M. Lattman, *Tetrahedron Letters*, 1974, 1709) dealing with the p.e. spectra of some 4-substituted pyridine *N*-oxides, where, however erroneous assignments were made.