

THE WAVENUMBERS OF NO₂ STRETCHING VIBRATIONS AND TRANSMISSION OF SUBSTITUENT EFFECTS IN 2- AND 4-SUBSTITUTED 3-NITROPYRIDINE SERIES

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The wavenumbers of both the symmetric and asymmetric stretching vibrations of the nitro group were measured in chloroform for the series of 2-X- and 4-X- substituted 3-nitropyridines as well as for *o*-X- substituted nitrobenzenes. The $\nu_{as}(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ values of both nitropyridine series were compared with those of corresponding nitrobenzenes. It has been found that the substituent effects in pyridines are transmitted to the 3-nitro group more readily from the 4-position, than from the 2-position. This transmission in 2-X- substituted 3-nitropyridines is comparable with that in the series of *o*-substituted benzene analogues. The transmission factors, γ , were determined according to Charton's definition for both 2,3- and 4,3-disubstituted pyridine rings. The separation of overall substituent effect into its inductive (field), resonance and steric components is discussed in terms of multiparameter correlation equations for wavenumber of asymmetric NO₂ stretching vibration.

The transmission of substituent effects in various series of disubstituted pyridines was investigated using several methods¹⁻³. However, only little attention has been paid to the structure-reactivity correlations in vicinally disubstituted pyridine derivative series. Brger⁴ and Tomasik⁵ have studied the polarographic reduction of a series of 2-substituted 3-nitropyridines, but they did not find any correlations between the reduction half-wave potentials and substituent constants. Recently a series of three papers has been prepared dealing with the correlations of the half-wave potentials of the one electron reversible reduction of the series of 2-X-substituted 3-nitropyridines and *o*-X-substituted nitrobenzenes⁶, 4-X-substituted 3-nitropyridines and 1-X-substituted 2,4-dinitropyridines⁷ and 3-X-substituted 2- and 4-nitropyridines as well as of their 1-oxides⁸. The wave numbers of the NO₂ stretching vibration of pyridine derivatives were also rarely studied. Only Tomasik^{8,9} attempted to correlate the wavenumbers of symmetric and asymmetric NO₂ vibrations against substituent constants in the solid-state spectra of the series of 2-substituted 5-nitropyridines. Both vibrations appeared to be rather insensitive to the substituent effects.

In this paper the transmission of substituent effects in the series of vicinally-substituted 3-nitropyridines is recognized based on the analysis of $\nu(\text{NO}_2)$ vibrations in their IR absorption spectra. For this purpose the wavenumbers of both the symmetric and asymmetric NO₂ stretching vibrations of 2-X-substituted (*I*) and 4-X-sub-

stituted 3-nitropyridines (*II*) were measured in chloroform and compared with those of *o*-X-substituted nitrobenzenes (*III*) measured in analogous conditions.

EXPERIMENTAL

Preparation of Compounds

Compounds in the series *I* and *II* except 4-N-methylnitramino-3-nitropyridine were prepared either by common or modified methods as given in our earlier papers^{6,7}.

4-N-Methylnitramino-3-nitropyridine. To a solution of 6.7 g (0.03 mol) of 3-methylamino-3-nitropyridine in 27 ml H_2SO_4 ($d = 1.83$) at -5°C 2.06 ml HNO_3 ($d = 1.52$) is added. The reaction mixture was allowed to stand for one hour in the room temperature and then poured onto the cracked ice. The precipitate is filtered off and crystallized from ethanol m.p. 210°C (decomp.) Yield: 2.25 g (26%). For $\text{C}_6\text{H}_6\text{N}_4\text{O}_4$ calculated: 36.37% C, 3.05% H, 28.28% N; found: 36.06% C, 3.38% H, 27.95% N. MS: m/z 198.

o-X-Substituted nitrobenzenes (*III*) were obtained from commercial sources and purified by standard methods. Some compounds of this series were prepared by means of modified literature methods⁶.

Spectral Measurements

The infrared spectra in CHCl_3 solutions were measured with a Zeiss Specord 75 IR spectrophotometer using 0.1 and 1.0 mm NaCl cells. Concentrations of the solutions were chosen to provide maximum of absorption of the bands examined between 70% and 80%. The peak positions with the accuracy of $\pm 0.5 \text{ cm}^{-1}$ are the average of three measurements. The instrument calibration was verified by using atmospheric water vapour and indene standard spectra.

RESULTS AND DISCUSSION

The wavenumbers of both the symmetric, $\nu_s(\text{NO}_2)$, and asymmetric, $\nu_{as}(\text{NO}_2)$, stretching vibrations for series of compounds *I–III* measured in CHCl_3 are listed in Table I.

Because of electron-withdrawing effects of the ring nitrogen atom the $\nu_s(\text{NO}_2)$ values of pyridine derivatives *I* and *II* are generally higher than those of corresponding benzene analogues (*III*). On the other hand this effect is much smaller in the case of asymmetric stretching vibration of the nitro group.

To investigate the transmission of overall substituent effects, in all the series correlations were attempted of the wavenumbers of both the symmetric and asymmetric NO_2 stretching vibrations versus σ_p and σ_p^+ substituent constants by simple Hammett and Brown equations, respectively. However, as it could be anticipated, in no case any satisfactory correlation was obtained. The identity criterion (in this case the relationship which compares the substituent effects in two of three series of nitro-compounds) delivers a reasonable way of elucidation of the transmission of substituent effects in the series under study. Thus the wavenumbers related to $\nu_s(\text{NO}_2)$

TABLE I

Wavenumbers (cm^{-1}) of $\nu_s(\text{NO}_2)$ and $\nu_{as}(\text{NO}_2)$ vibrations in CHCl_3 for series of 2-X-(I), 4-X-substituted (II) 3-nitropyridines and *o*-substituted nitrobenzenes (III)

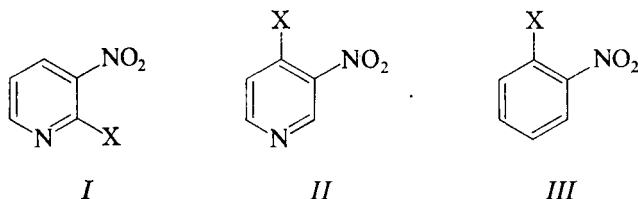
Compound	X	$\nu_s(\text{NO}_2)$	$\nu_{as}(\text{NO}_2)$
<i>Ia</i>	OH	1 350.5	^a
<i>Ib</i>	NHCOCH ₃	1 346.0	1 485.5
<i>Ic</i>	SCH ₃	1 344.0	1 513.0
<i>Id</i>	NH ₂	1 351.5	1 513.0
<i>Ie</i>	CN	1 348.5	1 536.0
<i>If</i>	NHNH ₂	1 357.0	1 516.5
<i>Ig</i>	NCH ₃ NO ₂	1 357.0	1 536.5
<i>Ih</i>	CH ₃	1 350.0	1 527.5
<i>Ii</i>	H	1 354.5	1 530.0
<i>Ij</i>	CONH ₂	1 370.0	^a
<i>Ik</i>	NHC ₆ H ₅	1 357.5	1 503.5
<i>Il</i>	F	1 351.0	1 536.0
<i>Im</i>	COOCH ₃	1 353.0	1 535.5
<i>In</i>	OCH ₃	1 351.0	1 527.0
<i>Io</i>	NHCH ₃	1 359.5	1 522.0
<i>Ip</i>	Cl	1 352.0	1 535.0
<i>Ir</i>	NHC(CH ₃) ₃	1 362.0	1 504.5
<i>Is</i>	Br	1 353.0	1 536.0
<i>It</i>	SC(CH ₃) ₃	1 336.5	1 513.0
<i>Iu</i>	NHNO ₂	1 353.5	1 543.0
<i>IIa</i>	NHCOCH ₃	1 346.5	1 494.5
<i>IIb</i>	SCH ₃	1 348.5	1 511.5
<i>IIc</i>	NH ₂	1 360.0	1 505.0
<i>IId</i>	CN	1 348.5	1 537.0
<i>IIe</i>	NHNH ₂	1 363.5	^a
<i>IIf</i>	CONH ₂	1 352.5	1 532.0
<i>IIg</i>	NHC ₆ H ₅	1 363.5	1 501.5
<i>IIh</i>	COOCH ₃	1 354.5	1 536.5
<i>IIi</i>	OCH ₃	1 357.0	1 528.0
<i>IIj</i>	NHCH ₃	1 367.5	1 520.0
<i>IIk</i>	NHC(CH ₃) ₃	1 370.0	1 521.5
<i>III</i>	SC(CH ₃) ₃	1 341.5	1 534.0
<i>IIIa</i>	SCN	1 345.0	1 523.5
<i>IIIa</i>	OH	1 333.5	1 478.0
<i>IIIb</i>	NHCOCH ₃	1 339.5	1 499.5
<i>IIIc</i>	SCH ₃	1 341.0	1 516.0
<i>IIId</i>	NH ₂	1 346.0	1 512.0
<i>IIIe</i>	CN	1 347.0	1 537.0
<i>IIIf</i>	NHNH ₂	1 347.5	1 517.0
<i>IIIg</i>	NCH ₃ NO ₂	1 349.0	1 536.5
<i>IIIh</i>	CH ₃	1 349.0	1 521.0

TABLE I
(Continued)

Compound	X	$\nu_s(\text{NO}_2)$	$\nu_a^a(\text{NO}_2)$
IIIi	C ₂ H ₅	1 350·0	1 522·5
IIIj	H	1 350·0	1 526·5
IIIk	CONH ₂	1 350·5	1 530·0
IIIl	NHC ₆ H ₅	1 350·5	1 503·0
IIIm	I	1 351·5	1 531·5
IIIn	F	1 351·5	1 534·0
IIIo	COOCH ₃	1 352·0	1 535·5
IIIp	OCH ₃	1 353·5	1 525·0
IIIr	NHCH ₃	1 354·0	1 516·0
IIIs	Cl	1 354·5	1 534·5
IIIt	NHC(CH ₃) ₃	1 355·0	1 506·0
IIIu	Br	1 356·0	1 534·5
IIIv	CH(CH ₃) ₂	1 359·5	1 521·5
IIIw	C(CH ₃) ₃	1 371·5	1 528·0

^a Low solubility.

and $\nu_{as}(\text{NO}_2)$ in the series I–III were compared using this criterion. The relevant results are quoted in Table II.



The $\nu_s(\text{NO})^I$ vs $\nu_s(\text{NO}_2)^{III}$ relationship spread into two correlations. Similar splitting is observed in the case of $\nu_s(\text{NO}_2)^{II}$ vs $\nu_s(\text{NO}_2)^{II}$ correlation (Fig. 1). In both correlations the points are distributed among the substituents capable formation of intramolecular hydrogen bonds with the NO₂ group (NHCOCH₃, NH₂, NHNH₂, NHC₆H₅, NHCH₃, NHC(CH₃)₃) and the substituents which cannot form such bonds (remained points). A similar splitting of ν_s vs σ correlations has been observed^{10–13} also in the case of other nitrocompound series. Moreover, the same correlation pattern could be observed¹⁴ in the case of identity criteria for the half-wave potentials of the polarographic reduction of the compounds series studied herein. This is of interest that the above-mentioned splitting is observed merely in the case of

symmetric vibrations of the nitro group. This fact is an additional proof for the intervention of the intramolecular hydrogen bond.

The slopes of $\nu(\text{NO}_2)$ vs $\nu(\text{NO}_2)^{\text{II}}$ correlations in the series *I* and *II* express immediately the values of transmission factors, γ , for vicinally disubstituted pyridine rings according to definition of Charton¹⁵ (Table II). The values of $\gamma(2,4\text{-Py})$ and $\gamma(4,3\text{-Py})$ for transmission of overall substituent effects from the 2- or 4-positions to the 3-position in the pyridine ring can be determined as the arithmetic means for both $\nu_{\text{as}}(\text{NO}_2)$ vs $\nu_{\text{as}}(\text{NO}_2)^{\text{III}}$ and $\nu_{\text{s}}(\text{NO}_2)$ vs $\nu_{\text{s}}(\text{NO}_2)^{\text{III}}$ correlations:

$$\gamma(2,3\text{-Py}) = 0.99 \quad \text{and} \quad \gamma(4,3\text{-Py}) = 1.31.$$

The comparison of above data reveals that the substituent effects in vicinally substituted 3-nitropyridines are transmitted to the nitro group more readily from the

TABLE II

Linear correlations $y = \rho x + q$ of wavenumbers of NO_2 stretching vibrations for compounds of series *I* and *II*

Series	y	x	n^a	r^b	ρ	q	s^c
<i>I</i> ^d	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{as}}(\text{NO}_2)^{\text{III}}$	15	0.976	1.01 ± 0.06	— 6.68	2.69
<i>I</i> ^e	$\nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)^{\text{III}}$	7	0.954	0.97 ± 0.14	45.17	1.75
<i>I</i> ^f	$\nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)^{\text{III}}$	8	0.949	0.58 ± 0.08	563.45	2.96
<i>II</i> ^g	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{as}}(\text{NO}_2)^{\text{III}}$	9	0.979	1.16 ± 0.09	— 242.19	3.44
<i>II</i> ^h	$\nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)^{\text{III}}$	7	0.970	1.47 ± 0.17	— 619.62	2.43
<i>II</i> ⁱ	$\nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)^{\text{III}}$	4	—	—	—	—

^a Number of points in the set. ^b Correlation coefficient. ^c Standard deviation. ^d Points representing compounds *Ib* and *Iu* (see Table I) are rejected from correlation, because of tautomerism. The remained points are omitted because of lack of relevant points in series *III*. ^e Only points for compounds bearing substituents capable formation of intramolecular hydrogen bond between NH and NO_2 groups ($\text{X} = \text{NHCOCH}_3, \text{NH}_2, \text{NHC}_6\text{H}_5, \text{NHCH}_3, \text{NHC}(\text{CH}_3)_3, \text{NHNH}_2$) and the parent compound ($\text{X} = \text{H}$) were subjected to correlation. ^f Points for remained compounds bearing substituents, which cannot form intramolecular hydrogen bond between NH and NO_2 groups, are used, except of compounds: *Ia* (because of intramolecular hydrogen bond between the OH and NO_2 groups), *Ig* (because of conformation induced by pyridine ring nitrogen atom) and *Ij* (because of intramolecular hydrogen bond between the NH_2 group and pyridine ring nitrogen atom). ^g Points representing compounds *Ile* and *Ilk—IIm* (see Table I) are omitted because of lack of relevant points in series *III*. ^h The same as in the case^e, except of the parent compound *Ii* ($\text{X} = \text{H}$) which does not fit this correlation, because in unsubstituted 3-nitropyridine is no *ortho*-effect. Additionally, compound *Iib* ($\text{X} = \text{SCH}_3$) for unknown reason follow just this correlation. ⁱ Not enough points to calculate the statistics of correlation, but the tendency is evident from the Fig. 1.

4-position than they are from the 2-position. The transmission from the 2-position is about the same as in the case of corresponding benzene analogues (*III*). This can be explained by the variation of the inductive-resonance composition of the interaction between the pyridine ring nitrogen atom and substituents, X, in 2- and 4-positions¹⁶. This interaction operates in compounds *II* in the same direction as the substituent effects are transmitted, while in compound *I* it has an opposite tendency.

Another approach to the quantitative evaluation of the substituent effects in *ortho*-disubstituted aromatic compounds accepts a separation of the overall substituent effects into inductive (field), resonance and steric components by means of multi-parameter correlation equations. Both the Taft's two-parameter and extended Hammett equations were frequently employed also in studying of the reactivity of various pyridine series^{1-8,16-20}. Following this approach we attempted to correlate both the $\nu_s(\text{NO}_2)$ and $\nu_{as}(\text{NO}_2)$ values for series *I-III* with selected and corrected σ_1 and σ_R^0 constants²¹ in the sense of Taft's two-parameter equation, however no statistically significant results were obtained. On the other hand the $\nu_{as}(\text{NO}_2)$ values for all three series (*I-III*) provide satisfactory correlations with field and resonance constants by Swain-Lupton equation (1).

$$\nu_{as}(\text{NO}_2) = \rho_{\mathcal{F}}\mathcal{F} + \rho_{\mathcal{R}}\mathcal{R} + h. \quad (1)$$

The modified \mathcal{F} and \mathcal{R} values were taken²² in these correlations. The results of statistical treatment are given in Table III.

The conclusion can be drawn from these results that in 3-nitropyridines both the field and resonance components of the overall substituent effect are transmitted better

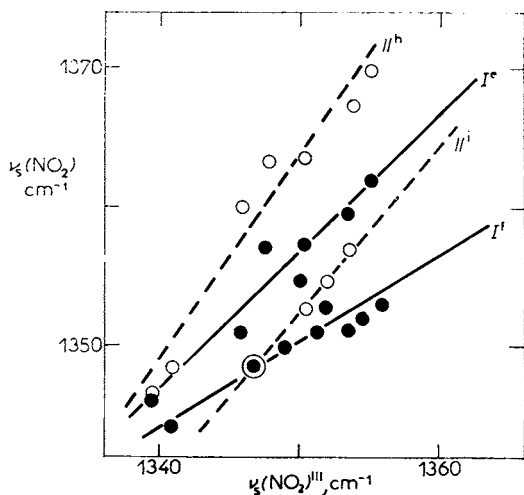


FIG. 1

The $\nu_s(\text{NO}_2)$ vs $\nu_s(\text{NO}_2)^{\text{III}}$ correlations; for compounds *I* — solid points and solid lines, for compound *II* — open points and broken lines. For other denotations see Table II

from the 4-position than from the 2-position. The contribution of the resonance effects to the correlations ($\% \mathcal{R}$) given by Eq. (2) is also listed in Table III.

$$\% \mathcal{R} = \frac{100\psi|\varrho_{\mathcal{F}}|}{\varphi|\varrho_{\mathcal{F}}| + \psi|\varrho_{\mathcal{A}}|} \quad (2)$$

The coefficients ψ and φ were calculated internally based upon the number of points, n , used in the correlations from Eqs (3) and (4)

$$\psi = (\sum|\mathcal{R} - \bar{\mathcal{R}}|)/n, \quad (3)$$

$$\varphi = (\sum|\mathcal{F} - \bar{\mathcal{F}}|)/n, \quad (4)$$

where $\bar{\mathcal{R}}$ and $\bar{\mathcal{F}}$ are the arithmetic means of resonance and field constants applied in the correlations. The magnitudes of $\% \mathcal{R}$ are almost identical for series *II* and *III* and close to 50. However, the contribution of resonance effects is considerably lower in the case of compounds *I*. It means that the inductive and field mechanism plays a significant role in the transmission of substituent effects. This can be due to electron-withdrawing effect of the ring nitrogen atom which operates most effectively in the vicinal-position in respect to X-substituents.

It has to be noted that no correlations have been found between the values of $\nu_s(\text{NO}_2)$ for the series *I–III* and Swain–Lupton \mathcal{F} and \mathcal{R} constants. Similar lack of correlation has been reported in the case of other nitro compound series^{10–13}.

TABLE III

Correlations of wavenumbers of asymmetric NO_2 stretching vibration for compounds of series *I–III* by the Swain–Lupton equation (1)

Series	n^a	r^b	$\varrho_{\mathcal{F}}$	$\varrho_{\mathcal{A}}$	h	s^c	$\% \mathcal{R}^d$
<i>I</i> ^e	9	0.949	15.72 ± 3.14	6.86 ± 2.45	1 529.07	2.91	34
<i>II</i> ^f	7	0.914	36.92 ± 33.53	20.97 ± 18.42	1 514.06	3.44	53
<i>III</i> ^g	15	0.905	20.53 ± 3.69	14.34 ± 2.60	1 525.79	3.57	48

^{a,b,c} See footnotes in Table II. ^d Calculated by Eq. (2). ^e Points for the compounds *Ie*, *Ih*, *Ii*, *Ie–Ip* and *Is* are correlated. ^f Points *IIIh–IIIk*, *IIIm*, *IIIo–IIIs* and *IIIu–IIIw* are subject to correlation. ^g Points *IIIa–IIIc*, *IIIl* and *IIIn* were rejected from correlation. The selection of the points for particular correlations results from the observations of the deviations. Points which significantly deviate are omitted.

To express more properly the transmission of substituent effects in vicinally substituted 3-nitropyridines and *o*-substituted nitrobenzenes also the steric component of the overall substituent effect should be considered. Thus the $\nu_{\text{as}}(\text{NO}_2)$ values were correlated by the three-parameter localized, delocalized, steric (LDS) equation reported by Charton³ (Eq. (5)).

$$\nu_{\text{as}}(\text{NO}_2) = L\sigma_I + D\sigma_R + S\nu + h. \quad (5)$$

Also corresponding two-parameter extended Hammett equation (Eq. (6)) was employed for comparison.

$$\nu_{\text{as}}(\text{NO}_2) = L\sigma_I + D\sigma_R + h. \quad (6)$$

In both Eqs (5) and (6) the inductive (σ_I), resonance (σ_R) and steric (ν) constants reported by Charton²³ were used.

In all series the points for compounds bearing substituents $X = \text{NHCOCH}_3$, NH_2 , NHNH_2 , NHC_6H_5 , $\text{NHC}(\text{CH}_3)_3$ and OH were rejected, because of their larger deviations from Eqs (5) and (6) caused by intramolecular hydrogen bonds between the NO_2 and NHR or NH_2 groups. The tautomerism takes additionally place in the case of compounds bearing $X = \text{OH}$ and NHCOCH_3 groups. The hydrogen bonds in the case of compounds *III* can be documented by^{24,25} and for pyridine derivatives (*I* and *II*) have been proved on the basis of our measurements in the region of N-H stretching vibrations²⁶. The deviations above-mentioned caused by intramolecular hydrogen bonds are also the case in the correlations of substituent effects on the half-wave potentials of polarographic reduction of vicinally substituted nitropyridines and their oxides⁶⁻⁸. The correlations according to Eqs (5) and (6)

TABLE IV

Correlation of wavenumbers of asymmetric NO_2 stretching vibration for compounds of series *I* and *III* by the LDS (5) and extended Hammett equation (6)

Series	n^a	r^b	L	D	S	h	s^c
<i>I</i> ^d	9	0.918	21.00 ± 5.92	11.10 ± 5.64	-11.53 ± 3.04	1 532.46	3.86
<i>I</i> ^d	9	0.626	19.07 ± 10.61	10.47 ± 10.14	—	1 526.27	6.94
<i>III</i> ^e	12	0.941	21.56 ± 2.77	8.37 ± 3.58	2.47 ± 2.35	1 523.58	2.38
<i>III</i> ^e	12	0.933	21.24 ± 2.77	9.13 ± 3.52	—	1 525.25	2.39

^{a,b,c} See footnotes in Table II. ^d Points for the compounds *Ie*, *Ig*–*Ii*, *II*, *In*, *Ip*, *Is* and *It* are considered. ^e Points for the compounds *IIIe*, *IIIg*–*IIIj*, *IIIm*, *III n*, *IIIp*, *III s* and *IIIu*–*IIIw* are correlated. Points which significantly deviate are omitted from correlations.

for compounds series *I* and *III* are given in Table IV. The relevant correlations for series *II* as well as for series *I* were statistically rather insignificant because of the small number of available compounds and therefore the results for series *II* were not quoted in Table IV and the results for series *I* should be considered with a limited deal of confidence.

The $\nu_s(\text{NO}_2)$ values for all three series correlate also neither by Eq. (5) nor Eq. (6).

Table IV shows that the efficiency of the transmission of inductive and resonance effects in series *I* is similar to that in series *III*, while the steric effects generally insignificant are exerted somewhat strongly in compounds *I*, than they are in *o*-substituted nitrobenzenes (*III*). This should be accounted for reduced distance between the X-substituent and the nitro group in *I* as a result of the change in bond lengths and valence angles compared to those in *o*-substituted nitrobenzenes (*III*).

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