Electric dipole moments of 2-halopicolines, their *N*-oxides, and 2-halo-4-nitropicoline *N*-oxides

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Dipole moment values of 2-halopicolines, their *N*-oxides, and 2-halo-
-4-nitropicoline *N*-oxides are calculated from the permittivity and refractive
indices measurements as well as by means of groups moments vectors. The
influence of substituents effects on the dipole moment values is discussed.

Вычислены стоимости дипольных моментов 2-галогенопиколинов,
их *N*-окисей и *N*-окисей 2-галогено-4-нитропиколинов из измерений
диэлектрических проницаемостей и показателей преломления света,
а также путем складывания векторов моментов групп. Рассмотрено
влияние индукционных и мезомерных моментов на стоимости дипольных моментов.

A great contribution to the examination of heterocyclic *N*-oxide structures
was submitted by *Linton* [1], who determined the dipole moment of pyridine
N-oxide and compared it with the dipole moments of aliphatic amine oxides. On
the basis of these examinations Linton found that the $N \rightarrow O$ bond has another
nature in heterocyclic amine *N*-oxides and independently of other authors
[2—8] he proved the presence of resonance structures consisting of the pyridine
N-oxide' molecule hybrid. The knowledge of resonance structures enabled the
explanation of susceptibility of heterocyclic *N*-oxides both to nucleophilic and
electrophilic substitution. This fact was also confirmed by examinations of
N-oxides of the pyridine series substituted in position 4 [8].

Investigation carried out by *Katritzky et al.* [8] confirmed the correctness of
Linton's [1] interpretation concerning the participation of different resonance
structures, because they proved the dipole moments of pyridine *N*-oxides sub-
stituted in position 4, independently of donor-acceptor nature of substituents,
to be always higher than the dipole moments of similarly substituted pyridine.

On the basis of dipole moments *Barnes* [9] calculated a susceptibility sequence
of three positions of the pyridine ring to electrophilic substitution as 4, 2, 3 or
2, 4, 3 and a charge density for an individual position in pyridine *N*-oxides.

Tsoucaris [10], when investigating dipole moments of *N*-oxides of the pyri-
dine series, trimethylamine *N*-oxide and their chlorides, found the lone electron

pair of oxygen atom to be connected with π-electrons of the pyridine ring so that the participation of double bond is 30 % in the N → O group.

Determination of the dipole moments proved to be helpful in the interpretation of electronic spectra, as it allowed to compare dipole moments calculated by PPP, CNDO, and INDO methods with those determined in experiments [11—20].

Cumper and *Vogel* [21] examined dipole moments of alkylpyridines in order to investigate hyperconjugation phenomenon and *Pushakavera* [22] determined dipole moments of pyridine, quinoline, phenazine, and acridine N-oxides in order to investigate how dipole moment values of heterocyclic compounds are being changed when transforming from monocyclic compounds to condensed systems.

Within extensive investigations on the reactivity of N-oxides of pyridine derivatives [25—36], 2-halopicoline N-oxides and their derivatives represent a considerable contribution [31—36]. Therefore it was useful to determine their dipole moments and to compare the results with those obtained previously. In addition, the results of dipole moment investigations, in spite of incompetitiveness of the measurements with regard to radiography or electronography in stereochemical investigations, can provide valuable preliminary information on molecule structures.

Experimental

Methods for preparation of compounds, the dipole moments of which are determined, were described earlier [34—36].

These compounds were dried thoroughly and their benzene solutions of various mass fractions were prepared in measuring flasks of 50 cm³ capacity. Then the permittivity (ε_r) of such prepared solution and benzene itself ($\varepsilon_{r,1}$) was measured by means of dipolemeter WTW Mod. DM 01 at the temperature 298 K. Prior to measurements the solutions and benzene were held in a thermostat during 15 min. At the same time in the same conditions measurements of refractive indices of the solutions (n_r) and benzene itself (n_1) were carried out by means of Abbe's refractometer, model G, with sodium vapour lamp.

The diagrams of the relationship $\varepsilon_r - \varepsilon_{r,1} = \Delta\varepsilon$ as a function of mass fraction (w) as well as diagrams of the relationship $n_r^2 - n_1^2 = \Delta n^2$ also as a function of mass fraction were constructed. Difference in slopes of the both straight lines ($\alpha - \gamma$) is included in the formula for calculation of experimental dipole moment value and is given in Table 1. The dipole moments listed in Table 1 are calculated for individual compounds from the formula

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Table 1

Dipole moment values of 2-halopicolines, their *N*-oxides, and 2-halo-4-nitropicoline *N*-oxides

Compound	$w \cdot 10^3$	$\alpha - \gamma$	$\dfrac{\mu_{exp}}{10^{-30} \text{ C m}}$	$\dfrac{\mu_{calc}}{10^{-30} \text{ C m}}$
2-Iodo-3-methylpyridine	0.1554—2.8270	3.267	8.57	10.77
2-Iodo-5-methylpyridine	0.3100—1.4300	6.357	11.94	11.54
2-Iodo-6-methylpyridine	0.5602—2.2430	3.311	8.64	10.44
2-Iodo-3-methylpyridine *N*-oxide	0.2426—1.9344	8.367	11.21	17.35
2-Iodo-5-methylpyridine *N*-oxide	0.2310—1.9290	9.102	14.81	17.85
2-Iodo-6-methylpyridine *N*-oxide	0.2169—1.9662	7.590	13.54	16.64
2-Iodo-3-methyl-4-nitropyridine *N*-oxide	0.0754—1.1910	0.950	5.24	4.77
2-Iodo-5-methyl-4-nitropyridine *N*-oxide	0.5503—1.9876	0.624	4.24	6.30
2-Iodo-6-methyl-4-nitropyridine *N*-oxide	0.2954—1.1480	0.620	4.21	5.67
2-Bromo-3-methylpyridine	0.1484—1.6359	5.190	9.57	11.21
2-Bromo-5-methylpyridine	0.4410—1.1600	8.116	11.98	12.01
2-Bromo-6-methylpyridine	0.4390—2.4510	2.595	6.77	10.94
2-Bromo-3-methylpyridine *N*-oxide	0.3500—1.1000	12.600	15.58	17.71
2-Bromo-5-methylpyridine *N*-oxide	0.3645—0.9423	17.080	18.15	18.25
2-Bromo-6-methylpyridine *N*-oxide	0.4626—1.4000	6.933	11.58	17.08
2-Bromo-3-methyl-4-nitropyridine *N*-oxide	0.4650—1.2000	2.640	7.94	5.30
2-Bromo-5-methyl-4-nitropyridine *N*-oxide	0.7049—1.2410	2.750	8.11	6.87
2-Bromo-6-methyl-4-nitropyridine *N*-oxide	0.1450—1.0380	0.479	3.44	6.24
2-Chloro-3-methylpyridine	0.3000—1.6000	8.404	10.48	11.24
2-Chloro-5-methylpyridine	0.1963—1.106	9.000	10.84	12.08
2-Chloro-6-methylpyridine	0.1800—1.6990	7.192	9.71	11.08
2-Chloro-3-methylpyridine *N*-oxide	0.1780—0.4170	18.840	16.65	17.79
2-Chloro-5-methylpyridine *N*-oxide	0.4570—1.3210	16.730	15.68	18.31
2-Chloro-6-methylpyridine *N*-oxide	0.1437—1.2383	17.500	16.05	17.15
2-Chloro-3-methyl-4-nitropyridine *N*-oxide	0.3860—1.0000	1.580	5.54	5.34
2-Chloro-5-methyl-4-nitropyridine *N*-oxide	0.4000—1.2100	1.186	4.80	6.94
2-Chloro-6-methyl-4-nitropyridine *N*-oxide	0.3003—0.7000	1.160	4.74	6.30

The values μ can be recalculated to the multiples D using the relationship $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}$.

$$\mu^2 = \frac{27kT}{4N\pi} \frac{M\varepsilon_0}{\varrho_1(\varepsilon_{r,1} + 2)^2} (\alpha - \gamma)$$

where k is the Boltzmann constant, N is Avogadro's constant, T temperature of measurement, ϱ_1 benzene density at 298 K, and M molar mass of a compound examined.

Results and discussion

The dipole moments of 2-halopicolines, their N-oxides, and 2-halo-4-nitro-picoline N-oxides were calculated from the permittivity and refractive indices measurements as well as by means of vectorial model [37].

The dipole moments of 2-halopicolines, which have been measured during investigations carried out, oscillate in the range $(6.77—11.98) \times 10^{-30}$ C m. The lowest values are attributed to iodine derivatives, next values are attributed to the bromine ones and the highest values belong to chlorine derivatives, which is in accordance with the halogen inductive effect. A halogen characterized by the inductive effect higher than the mesomeric one, introduced to the molecule, caused the withdrawal of electrons from the nitrogen atom; thus the dipole moment is decreased. The dipole moments of halopyridines are lower than the dipole moment of pyridine [25]. 4-Halopyridines have the lowest dipole moments, because of more effective attraction of electrons by halogen, due to the ring mesomerism.

The methyl group exerts also an influence on the dipole moment of halo-picolines. Its highest influence can be observed in position 5, which can be explained by electron density increase on the carbon atom in position 2, connected with transposition of the methyl group inductive effect by mesomerism. Somewhat lower dipole moment is attributed to the derivatives with methyl group in position 3, which can be associated with space obstacles (causing mesomerism inhibition) and with hyperconjugation. The dipole moments of 2-halo-6-methylpyridines have somewhat lower values than those of 2-halo-3-methyl-pyridine (difference oscillates in the range $(-0.07—2.80) \times 10^{-30}$ C m, because of the steric factor and possibility of formation of hydrogen bond between nitrogen and hydrogen of the methyl group).

The dipole moments of 2-halopicoline N-oxides oscillate in the range $(11.58—18.15) \times 10^{-30}$ C m. Such high moments belong to amphoteric ions. Such a structure would be reasonable because the amphoteric structure system is preferential when at the same time an electron-donating group (*e.g.* halogen) and electron-attracting group (*e.g.* N-oxide group) are connected with the aromatic system.

The dipole moment values of 2-halopicoline N-oxides are close to the values

of the dipole moment of trimethylamine N-oxide, where the $N \rightarrow O$ bond is semipolar. The high dipole moment values of 2-halopicoline N-oxides and their comparison with the dipole moment values of 2-halopicolines point out a high inductive effect I^- on the N-oxide group and connected with this fact susceptibility of the halogen in position 2 to nucleophilic substitution. It was stated previously that 2-halopicoline N-oxides are much more reactive in the reaction with sodium alkoxide than 4-nitro derivatives but much less reactive with weak nucleophiles (amines) [31].

Reactivity of 2-halopicoline N-oxides, resulting from measurements of dipole moments, shows good conformability with the reactivity of compounds assumed on the basis of thermodynamic constants calculated from the reaction rate constants [34].

Derivatives including the methyl group in position 5 have the highest dipole moments and the highest activation energy value, because the methyl group in position 5 coupled with a halogen in position 2, increases the electron density at C-2, which affects the decrease of halogen reactivity with a nucleophilic reagent.

Considerable decrease of the dipole moments is observed after introducing the nitro group to position 4 of pyridine ring. The nitro group having a strong inductive effect I^- and a strong mesomeric effect M^-, exerts in position 4 such a great influence that the N-oxide group in its presence becomes an electron-donating group. In 2-halo-4-nitropicoline N-oxides the influence of quinoid structure becomes essential. The dipole moment values of 2-halo-4-nitropicoline N-oxides are lower than those of 2-halopicolines and some of them are even lower than the dipole moment of pyridine and oscillate in the range $(3.44—8.11) \times 10^{-30}$ C m. This can prove an arrangement which is required by the optimum action of electrons with a substituent.

Among 2-halo-4-nitropicoline N-oxides the iodo derivatives are characterized by the lowest dipole moment values, the next are chloro and bromo derivatives. In the group of 2-halopicolines, their N-oxides, and 2-halo-4-nitropicoline N-oxides including the same halogen atom, the highest dipole moment values belong to derivatives containing the methyl group in position 5. The influence of halogen atom and methyl group on dipole moment values of the compounds described in this paper was already discussed previously (on example of 2-halopicolines), however, they have not such a considerable influence as that of N-oxide and nitro groups. Infrared spectra also prove an influence of mesomeric effect of nitro group on the dipole moment of 2-halo-4-nitropicoline N-oxides. The bands corresponding to the stretching vibration of N-oxide group are at $\tilde{v} = 1265$ cm^{-1} in pyridine N-oxide [21] and at $\tilde{v} = 1303$ cm^{-1} in 4-nitropyridine N-oxides and they oscillate in the range of $\tilde{v} = 1277—1297$ cm^{-1} in 2-halopicoline N-oxides.

In the scope of this work also the dipole moments of the studied compounds are calculated by the method of calculus of vectors and it was proved that these values are mostly higher than the experimental values and they do not show good conformability. This fact is not a surprise, because the dipole moment calculated even for a compound containing a substituent with low mesomeric and inductive effect, was not identical with the dipole moment determined in an experiment [24]. The cause of inconformability can be moments induced by every substituent in the neighbouring constituent and in the aromatic molecule. *Sharpe* and *Walker* [24] calculated the moments of alkyl compounds, taking into consideration the inductive effect and they obtained dipole moment values close to the experimental ones, however, not in all cases the conformability was satisfactory.

The difference between the experimental value and that calculated by the method of calculus of vectors, is a measure of inner interaction of substituents in a molecule. This value oscillates for 2-halopicolines in the range (-4.17 —0.40) $\times$ 10^{-30} C m, for 2-halopicoline N-oxides in the range (-5.50 to -0.10) $\times$ 10^{-30} C m and for 2-halo-4-nitropicoline N-oxides in the range (-2.80—2.64) $\times$ 10^{-30} C m. These calculations do not take into consideration mutual interaction of a halogen in position 2 with the nitrogen atom, methyl group, and the ring in the case of 2-halopicolines and mutual interaction of a halogen in position 2 with N-oxide and methyl groups in the case of 2-halopicoline N-oxides. Comparison of difference values between experimental dipole moment values and those calculated for 2-halopicolines ((-4.17—0.40) $\times$ 10^{-30} C m and (6.67—11.98) $\times$ 10^{-30} C m) as well as for 2-halopicoline N-oxides ((-5.50 to -0.10) $\times$ 10^{-30} C m and (13.54—18.15) $\times$ 10^{-30} C m) shows better conformability for 2-halopicolines. (2-Bromo-6-methylpyridine N-oxide is an exception.) The presence of four substituents in pyridine ring in 2-halo-4-nitropicoline N-oxide is a reason, as it should be expected, for still worse conformability of experimental dipole moment with the calculated one, which is proved by difference value between experimental dipole moment value and the calculated dipole moment value ((-2.80—2.64) $\times$ 10^{-30} C m) with regard to their experimental dipole moments ((3.44—8.11) $\times$ 10^{-30} C m).

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