

# Electric dipole moments of 2,4-dihalopicolines and their *N*-oxides

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Dipole moment values of 2,4-dichloro- and 2,4-dibromopicolines and their *N*-oxides were calculated from the permittivity and refractive indices measurements as well as by means of composition of groups and bonds moments vectors. The influence of substituents effects on the dipole moment values was discussed and the results obtained were compared.

Вычислены стоимости дипольных моментов 2,4-дигалогенопиколинов и их *N*-окисей 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.

2,4-Dihalopicolines (halogen = Cl, Br) and their *N*-oxides were prepared in order to determine their dipole moments [1, 2]. Investigations carried out by Linton [3], Katritzky [4], and Barnes [5] dealt with the contribution of different resonance structures forming the pyridine *N*-oxide hybrid and with susceptibility of different pyridine ring positions to electrophilic and nucleophilic substitution. Tsoucaris [6] found that the double bond contribution in N → O group of pyridine *N*-oxide is 30%.

Recent investigations deal with quantum-chemical calculations of heterocyclic compounds dipole moments [7–15]. A comparison of dipole moment values of some heterocyclic compounds calculated by means of PPP, CNDO, and INDO methods with the experimental dipole moment values of the same compounds enabled to go deeper into the molecule structure. Cumper and Vogel [16] have determined the dipole moments of the alkyipyridines in order to examine the hyperconjugation phenomenon.

Recently the dipole moments of 3-halo-2,6-dimethylpyridines and their *N*-oxides as well as 3-halo-4-nitro-2,6-dimethylpyridine *N*-oxides (halogen = F, Cl, Br, I) [17] and 2-halopicolines (halogen = Cl, Br, I) and their *N*-oxides [18] have been measured. The comparison of experimentally determined dipole moments of the above-mentioned compounds with those calculated from the group and bond moments provided valuable information about the interaction

between a substituent and ring (this is particularly important if a substituent is conjugated with  $\pi$ -electrons of the pyridine ring).

The determination of the dipole moments of 2-halopicolines and their *N*-oxides as well as of 2-halo-4-nitropicoline *N*-oxides provided a valuable information about the substituents effects and molecular structure. A high increase in dipole moment value when going from 2-halopicolines to their *N*-oxides reveals a high inductive effect of the *N*-oxide group but a considerable decrease of dipole moment value in 2-halo-4-nitropicoline *N*-oxides is an evidence of coplanar arrangement of the nitro group in the molecule. Preparation of the studied compounds developed new possibilities for experimental determination of dipole moments, because it is interesting how a halogen situated in position 4 affects other substituents in the ring and particularly the N  $\rightarrow$  O bond character.

## Experimental

Preparation of the compounds has been described in Refs. [1, 2]. The whole procedure of measurement and calculation is identical with that given in paper [18]. The obtained values are presented in Table 1.

## Results and discussion

The dipole moments of 2,4-dihalopicolines and their *N*-oxides were calculated from the permittivity and refractive indices measurements as well as by means of composition of group and bond moments. Group and bond moment values were taken from a reference list [19]. The difference between the experimental dipole moment and that calculated by means of vector calculus is a measure of inner interaction of substituents with each other as well as their interaction with the ring. The experimental dipole moment values are for the most part higher than the moments calculated by the vector calculus and they oscillate within  $(11.90\text{--}14.64) \times 10^{-30}$  C m and  $(6.73\text{--}9.34) \times 10^{-30}$  C m limits, respectively. 2,4-Dihalopicolines have lower dipole moment values than 2-halopicolines [17]. Similarly 4-chloropyridine has a considerably lower dipole moment ( $2.33 \times 10^{-30}$  C m) than pyridine ( $7.40 \times 10^{-30}$  C m) because the dipole moment of the chlorine atom acting on the same axis as dipole moment of the nitrogen atom, is oppositely directed. The dipole moment values of 2,4-dibromopicolines are higher than those of the respective dichloro derivatives. This is presumably due to a higher mesomeric effect of the bromine atom.

Methyl group does not exert great influence on the dipole moment of the molecule. The dipole moments of 2,4-dihalopicoline *N*-oxides are considerably

Table 1

Electric dipole moments  $\mu$  of 2,4-dihalopicolines and their *N*-oxides

| Compound                                      | Mass fraction<br>$w \cdot 10^3$ | $\alpha^a$ | $\gamma^a$ | $\frac{\mu_{\text{exp}}^a}{10^{-30} \text{ C m}}$ | $\frac{\mu_{\text{calc}}^a}{10^{-30} \text{ C m}}$ |
|---|---------------------------------|------------|------------|---|--|
| 2,4-Dichloro-3-methylpyridine                 | 0.239—0.775                     | 5.80       | 1.90       | $8.04 \pm 0.03$                                   | 6.44   |
| 2,4-Dichloro-5-methylpyridine                 | 0.250—1.560                     | 7.14       | 3.06       | $8.24 \pm 0.03$                                   | 7.80   |
| 2,4-Dichloro-6-methylpyridine                 | 0.285—1.690                     | 4.12       | 0.70       | $7.54 \pm 0.02$                                   | 7.00   |
| 2,4-Dibromo-3-methylpyridine                  | 0.200—1.610                     | 3.75       | 0.86       | $8.64 \pm 0.03$                                   | 6.40   |
| 2,4-Dibromo-5-methylpyridine                  | 0.280—1.300                     | 4.30       | 0.90       | $9.34 \pm 0.02$                                   | 6.80   |
| 2,4-Dibromo-6-methylpyridine                  | 0.266—0.863                     | 3.40       | 1.64       | $6.74 \pm 0.03$                                   | 5.27   |
| 2,4-Dichloro-3-methylpyridine <i>N</i> -oxide | 0.227—0.722                     | 13.36      | 1.60       | $14.64 \pm 0.03$                                  | 12.61  |
| 2,4-Dichloro-5-methylpyridine <i>N</i> -oxide | 0.503—1.243                     | 9.42       | 1.66       | $11.91 \pm 0.03$                                  | 13.38  |
| 2,4-Dichloro-6-methylpyridine <i>N</i> -oxide | 0.282—1.251                     | 11.43      | 1.13       | $13.71 \pm 0.02$                                  | 12.24  |
| 2,4-Dibromo-3-methylpyridine <i>N</i> -oxide  | 0.683—1.251                     | 8.00       | 1.21       | $13.64 \pm 0.03$                                  | 12.64  |
| 2,4-Dibromo-5-methylpyridine <i>N</i> -oxide  | 0.308—1.140                     | 8.49       | 2.41       | $12.93 \pm 0.03$                                  | 13.38  |

a) See Ref. [18].

higher than those of their parent bases (it looks analogically if the dipole moments of 2-halopicolines and their *N*-oxides are compared [18]). There is an evidence of great inductive effect of the *N*-oxide group and a susceptibility to nucleophilic substitution of a halogen situated in position 2, connected with this effect.

The difference between experimental values and those calculated by vector calculus for 2,4-dihalopicolines oscillates within  $(0.63—2.33) \times 10^{-30} \text{ C m}$  limits and for their *N*-oxides within  $(-1.47—2.03) \times 10^{-30} \text{ C m}$  limits and it is a measure of interaction between halogen atoms situated in position 2 and 4 as well as of their interaction with the methyl group, *N*-oxide group, and with the pyridine ring.

Nitro group situated in position 4 decreases dipole moment values much more than a halogen atom in this position. Evidence of this phenomenon are the following dipole moment values

$$\mu(2\text{-bromo-3-methyl-4-nitropyridine } N\text{-oxide}) = 5.30 \times 10^{-30} \text{ C m}$$

$$\mu(2,4\text{-dibromo-3-methylpyridine } N\text{-oxide}) = 13.64 \times 10^{-30} \text{ C m}$$

$$\mu(2\text{-bromo-3-methylpyridine } N\text{-oxide}) = 15.58 \times 10^{-30} \text{ C m}$$

Both the dipole moment of nitro group situated in position 4 and of a halogen in the same position act along the same axis as the dipole moment of *N*-oxide group, but their senses are oppositely directed. This affects the dipole moment

decrease for 2-halo-4-nitro- and 2,4-dihalopicoline *N*-oxide in relation to 2-halopicoline *N*-oxide. However, the nitro group in position 4 having strong inductive effect and strong mesomeric effect  $M^-$  exerts so strong influence that the *N*-oxide group becomes an electron-delivering one at its presence. In the case of 2-halo-4-nitropicoline *N*-oxides the contribution of quinoid structure grows important and this is an evidence of the nitro group and ring coplanar arrangement.

The dipole moment values of 2,4-dibromopicoline *N*-oxides — higher than those of the respective dichloro derivatives — are connected with a higher mesomeric effect value of bromine.

The dipole moments of 2,4-dihalo-5-methylpyridine *N*-oxides are the lowest, because a close neighbourhood of methyl group having negative inductive effect on a halogen in position 4 increases the dipole moment of this halogen. This fact causes a decrease of dipole moment because the dipole moment senses of the halogen in position 4 and those of *N*-oxide group are oppositely directed. The methyl group situated in position 3 is influenced by a halogen situated in position 2 or 4 and exerts smaller influence on dipole moment of the molecule.

Determination of the experimental dipole moment values of 2,4-dihalopicoline *N*-oxides enabled to state that the halogen situated in position 4 decreased semipolar bond contribution of the *N*-oxide group, resulting in polarity decrease of the above-mentioned compounds compared with 2-halopicoline *N*-oxides.

The dipole moment values of 2,4-dihalopicolines and their *N*-oxides calculated by vector calculus differ from the experimental ones. This cannot be a surprise, since even for disubstituted benzene *ortho* derivatives the dipole moments calculated by vector calculus are not in good conformity with the experimental values in contradistinction to the dipole moments of *meta* and *para* isomers [15]. The reason of the mentioned divergence may be dipole moments induced by each substituent in the adjacent substituent and in the aromatic part of the molecule.

Moreover, the bond lengths and angles in pyridine (and presumably in pyridine *N*-oxides) differ from those in benzene. This difference is certain to mean differing electronegativities of the ring carbon atoms in the two systems and this in turn will affect both the C—X group dipole moment and unsubstituted C—H group moments [10]. *Sharpe* [20] thinks that it is unwise to expect the calculated moment, even for a substituent with a low mesomeric and inductive effect, to be identical with the moment observed. Allowances for electric induction appear to point towards better accordance [21].

Calculation of dipole moments for 2,4-dihalopicolines and their *N*-oxides does not take into account strong influence of halogen atom situated in positions 2 and 4, various mesomeric interactions with *N*-oxide group and methyl

group in positions 3, 5 or 6 and with the ring as well as the effect of solvent and ability of mentioned compounds to form self-complexes.

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