

*Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary*

PYRYLIUM SALTS WITH LONG ALKYL SUBSTITUENTS HAVING A TERMINAL FREE AMINO GROUP. CORROSION INHIBITORS DERIVED FROM CORRESPONDING PYRIDINIUM SALTS **

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Four N-ethyleneamino-pyridium hydrochlorides with varying alkyl side chains were prepared. The effectiveness of these as corrosion inhibitors for steel in acidic water was investigated and the results compared with untreated water.

The experimental results demonstrated that the pyridinium products offered protection for OL37 steel and show promise as an inhibiting system in aggressive environments.

Experimental protocol and various corrosion conditions are given.

The water and N-ethyleneamino-pyridium hydrochlorides analysis was performed by modern physical-chemical methods (hardness, organic compounds and inorganic salts contents, conductivity, ¹H and ¹³C-NMR, IR, UV-Vis, AE).

INTRODUCTION

In previous paper¹ we described the synthesis and surfactant properties of pyridinium perchlorates with long alkyl substituents having free ethyleneamino terminal group.

Converting otherwise insoluble amines into their hydrochlorides is a common way to make them water and acid-soluble. This is particularly desirable for substances used in medications. Many pharmaceutical substances used are prepared as hydrochlorides so that they may be quickly absorbed in the gastrointestinal tract. The typical breadth of time needed for a hydrochloride to be absorbed thusly is 15-30 minutes.²

Many corrosion inhibitors are available to protect ferrous and non-ferrous metals, for a variety of conditions including humidity and

aggressive agents, as well as corrosive industrial,³ marine and tropical atmospheres. Some corrosion inhibitors are hexamine, phenylenediamine, dimethylethanolamine, sodium nitrite, condensation products of aldehydes and amines (imines), chromates, nitrites, phosphates, hydrazine, ascorbic acid and others.⁴

A new class is migrating corrosion inhibitors (MCI). These inhibitors can be organic or inorganic compounds and was developed to protect the embedded steel rebar/concrete structure. Organic inhibitors forming a monomolecular film between the metal and the water. In the case of film-forming amines, one end of the molecule is hydrophilic and the other hydrophobic. These molecules will arrange themselves parallel to one another and perpendicular to the reinforcement such that a continuous barrier was formed.⁵

** This is contribution no. 12 in the series “Pyrylium Salts with Long Alkyl Substituents”. For some previous papers in this series see ref. ^{1, 8-16}

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Pyridinium salts have many technical applications and were mentioned to be anticorrosive agents.⁶

So, the influence of pyridinium chloride and n-hexadecyl pyridinium chloride on the corrosion of mild steel in 5N HCl and 5N H₂SO₄ has been studied using techniques such as weight loss measurements and a relationship between the structure of the compounds under study and their corrosion-protective properties was revealed.⁷

More other fifty new 2,4,6-trisubstituted / 2,3,4,6-tetrasubstituted pyridinium salts having either one, or two linear α/γ -alkyl side chains, which are expected to be useful as efficient transfection vectors in gene therapy were obtained in our laboratory in the last years.⁸⁻¹⁶

The present paper describes the synthesis of 2,4,6-trisubstituted pyridinium hydrochlorides having one or two various linear and long side chains in 2,6-positions. An experimental procedure, spectral data and elemental analyses for the new compounds are presented.

Pyridinium hydrochlorides with long alkyl substituents were prepared in quantitative yields from the reaction of hydrochloric acid with corresponding pyridinium salts having a free amino terminal group. All these compounds are soluble in usual solvents such as lower alcohols, acetone and chloroform.

These novel hydrochlorides are expected to be useful as corrosion inhibitors.

Some of the most notable results in the field of the influence of pyridium salts effect on corrosion process are reported in this paper. Thus, the corrosion rate for OL 37 steel in acidic water was relatively large. When corrosion experiments were carried out with N-ethyleneamino-pyridium hydrochlorides with long alkyl side chains **1a-d**, good results were obtained. The dependence of corrosion rate in time (1 hour–90 days) with type and concentration of organic compound, was presented.

RESULTS AND DISCUSSION

Preparation and spectra of N-ethyleneamino-pyridium hydrochlorides

The synthesis of pyridinium salts with long alkyl substituents having free ethyleneamino terminal group has been described in detail elsewhere.¹

Pyridinium hydrochlorides were conveniently prepared by reaction of hydrochloric acid with corresponding pyridinium salts having a free amino terminal group. After drying and concentration, the hydrochloride salts **1a-d** in yields higher than 97% were obtained. **Figure 1** presents the various compounds which are relevant for this study.

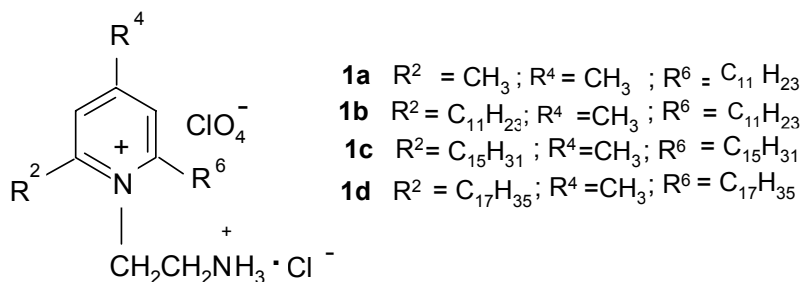


Fig. 1 – Pyridinium hydrochlorides with long alkyl substituents.

The synthesis, elemental analysis and spectral characterization of **1a-1d** are described as follows.

All new compounds were fully characterized by ¹H- and ¹³C-NMR, by IR spectra as well as elemental analysis.

NMR spectra

The ¹H- and ¹³C-NMR (at 400 MHz for protons and at 100 MHz for carbons) were recorded on BRUKER AVANCE DRX 400 spectrometer in CDCl₃.

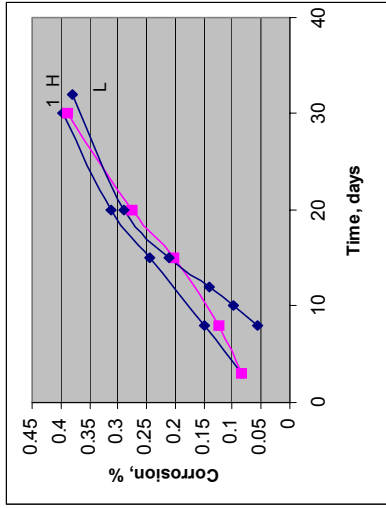
The ¹H and ¹³C-NMR chemical shifts of pyridinium salts **1a-d** were in agreement with the previously reported NMR data on the 2,4,6-trisubstituted homologs^{1,8-16} and are collected in **table 1**. The assignment of the proton signal is in all cases straightforward. Unambiguous assignments for **1a-d** were accomplished using two-dimensional correlation spectroscopy (COSY, HMQC and HMBC). **Table 1** presents the proton and carbon chemical shifts and should allow an easy comparison of the data.

Table 1

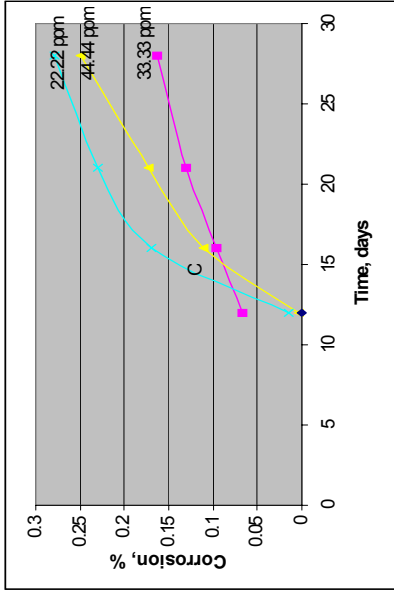
Selected signal assignments for ^1H and ^{13}C -NMR spectra for compounds 1a-1d

| Cpd. | ^1H and ^{13}C chemical shifts $\delta(\text{ppm})$ in CDCl_3 . | | | | | | | | | | | | | | |
|-----------|--|-----------------|--------------|------------------|--------------|------------------|------------------------|--------------------------------|--------------------------------|--------------------------------|--|--|--|-----------------------------------|--------------------------------|
| | Aromatic ring | | | | | | Aliphatic substituents | | | | | | | | |
| | 2C | 3C* | 4C | 5C* | 6C | 4CH ₃ | 6CH ₃ | 1 ^o CH ₂ | 2 ^o CH ₂ | 3 ^o CH ₂ | 4 ^o - (n ^o -2)CH ₂ | (n ^o -2) CH ₂ * | (n ^o -1) CH ₂ | 1 ^o CH ₂ | 2 ^o CH ₂ |
| 1a | -/ 158.35 | 7.54/ 127.71 | -/ 159.76 | 7.70 / 130.10 | -/ 155.29 | 2.75/ 21.67 | 2.91/ 21.53 | 3.22/ 32.92 | 1.77/ 29.35 | 1.40- 1.44/- | 1.26-1.38/- | -/ 29.67 | -/ 22.62 | 5.16/ 51.10 | 4.94/ 43.20 |
| 1b | -/ 160.80 | 7.68/ 125.77 | -/ 161.19 | -/ - | -/ - | 2.57/ 22.66 | -/ - | 3.17/ 32.88 | 1.80/ 29.08 | 1.46- 1.49/- | 1.25-1.40/- | -/ 29.66 | -/ 22.67 | 5.10/ 49.89 | 4.18/ 42.60 |
| 1c | -/ 159.20 | 7.69/ 126.04 | -/ 159.80 | -/ - | -/ - | 2.58/ 22.69 | -/ - | 3.20/ 32.90 | 1.79/ 29.07 | 1.47- 1.49/- | 1.25-1.40/- | -/ 30.16 | -/ 22.98 | 4.89/ 49.99 | 4.22/ 42.80 |
| 1d | -/ 159.33 | 7.65/ 126.02 | -/ 159.79 | -/ - | -/ - | 2.58/ 22.69 | -/ - | 3.21/ 32.93 | 1.79/ 29.08 | 1.47- 1.49/- | 1.25-1.40/- | -/ 30.40 | -/ 22.98 | 4.89 49.93 | 4.24/ 42.88 |

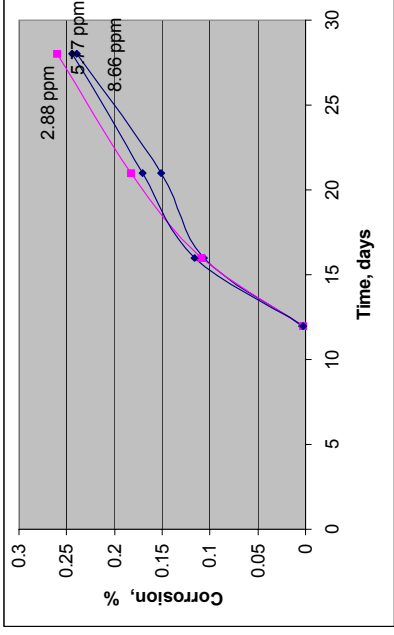
*assignment based by H-C 2D spectra



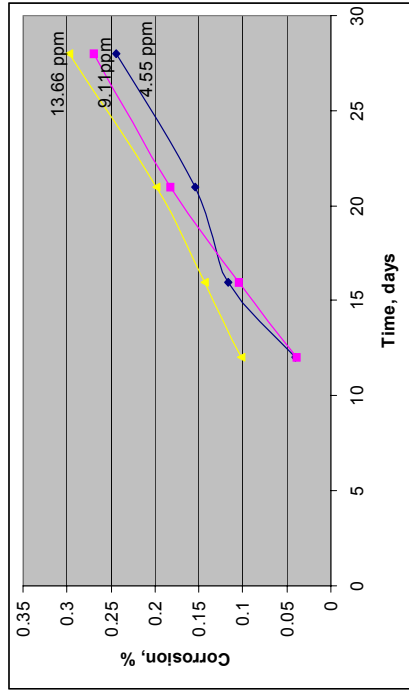
2.0



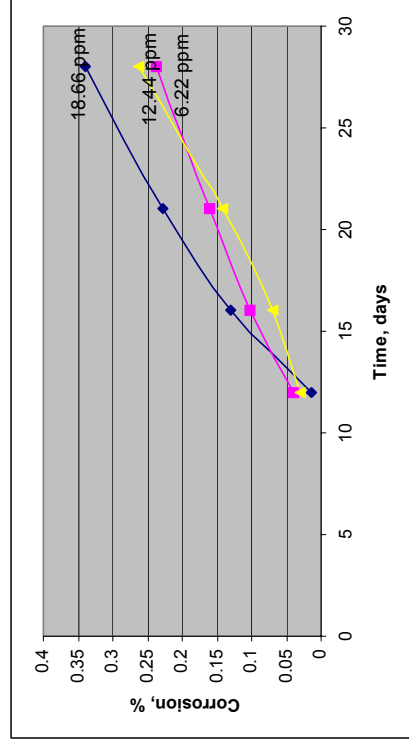
2.a



2.b



2.c



2.d

Fig. 2 – The variation of corrosion rate in time using 1a-d.

Most of the signals for **1a-d** were similar to that observed for analogue pyridinium salts having a free amino terminal group. Somewhat different chemical shifts values for 3H/ 5H heterocyclic ring and the first alkyl side chain protons were observed. So, 5H for **1a** and 3H for **1b-1d** is the most deshielded proton. It appears as a singlet at 7.70 and 7.65 -7.69 ppm, respectively. Comparasson of spectral data within **1a-d** and corresponding pyridinium salts having a free amino terminal group indicates that the different anion/dianion electronegativity was responsible for differentiated ¹H-NMR and ¹³C-NMR spectra.

IR spectra

We studied in this paper the effect of chemical structure in the IR spectrum of **1a-d**. Thus, ν (cm⁻¹) was slightly shifted to the larger values than in the starting compounds and a new medium intensity band, specific to hydrochlorides salts (assigned to au overtone) appears at 2560-2570 cm⁻¹.

The corrosion experiments

The determination of OL37 plates corrosion was carried out with the gravimetric method in statical conditions, at room temperature, using a "work" water derived from Arges river. The physical-chemical water's properties were described as follows (**Table 2**).

Corrosion experiments were carried out with **1a-d** and different concentrations (4-50 ppm), in closed flask. The dependence of corrosion rate in time (1 hour-90 days) with type and concentration of organic compound, was also studied.

The OL37 steel plates were exposed to corrosive acidic medium under constant immersion and alternating wet and dry immersion. Measurements consisted of monitoring the steel resistance as a function of exposure time and visual

examination of the adherence and corrosion of the surface.

Hydrochloric acid is the most corrosive agent for OL37 steel. Initial corrosion studies with "work" water without pyridinium salts with long alkyl substituents revealed (**figure 2.0**) that this acidic water caused a rapid corrosion of OL37 plates.

Futher addition of **1a-d** (4-50 ppm) in the composition of "work" water leading to decrease the corrosion rate.

Figures 2a-d shows the corrosion rate as a function of time and for three concentrations of pyridinium salts **1a-d**. So, the corrosion rate (%) for **1a-d** shows an initial increase with time for all concentration, followed by an decrease to a constant value (after 30 days).

The difference for **1a** (one long side chain) and **1b-d** (two long side chains) is thus very likely attributed to the effect of coalescing compound on the surface film. These results are consistent with the correlation of the surface film forming with the increased compounds hydrobicity. It is interesting to note that doubling or tripling the concentration of **1a** does not appear to have a significant impact on corrosion. In the case **1b-d** all corrosion tests were conducted at low concentrations. Experimental results indicated that the long alkylpyridinium salts **1c** and **1d** were found to be the best inhibitors. These compounds generated quite similar corrosion curves as one observes by comparing **figure 2b**, **2c** and **2d**.

EXPERIMENTAL PART

Materials and methods

The physical-chemical water's properties were:

The base water was derived from Arges river at the CET Vest enter. The physical-chemical water's properties were presented in **table 2**:

Table 2

The physical-chemical water's properties

| No. | Determination | U.M. | Value |
|-----|--|----------------|-------|
| 1 | Boiling point | ⁰ C | 97 |
| 2 | Total hardness | mval/l | 3 |
| 3 | Temporary hardness | mval/l | 2.1 |
| 4 | Fixed residue | mg/l | 128 |
| 5 | Content in organic compounds | mg/l | 23.7 |
| 6 | Content in SiO ₂ | mg/l | 6 |
| 7 | Content in Ca ²⁺ | mg/l | 38.1 |
| 8 | Content in Mg ²⁺ | mg/l | 10.4 |
| 9 | Content in Na ⁺ | mg/l | 4.1 |
| 10 | Content in K ⁺ | mg/l | 0.1 |
| 11 | Content in HCO ₃ ⁻ | mg/l | 55.4 |

Table 2 (continues)

Table 2 (continued)

| | | | |
|----|--|-------|-------|
| 12 | Content in Cl ⁻ | mg/l | 8.0 |
| 13 | Content in SO ₄ ²⁻ | mg/l | 8.7 |
| 14 | Content in PO ₄ ³⁻ | mg/l | 0.04 |
| 15 | Conductivity | µs/cm | 270 |
| 16 | pH _i (initial) | - | 6-6.5 |
| 17 | pH _w (work) | - | 3-3.5 |

Procedures

Synthesis of *N*-ethyleneamino-pyridinium hydrochlorides **1a-d**.

Pyridinium hydrochlorides salts **1a-d** were prepared according to the following general procedure: to the solution of corresponding pyridinium perchlorate having free amino terminal group in methylene chloride, an excess of HCl 6% were added (molar ratio 1:5). The mixture was stirred for one hour. After solvents evaporation and dried in a vacuum oven, waxy oils which crystallized in refrigerator (m.p.=19.5-20.5 °C for **1a** and m.p.=22-23 °C for **1b**) or waxy oil (for **1c** and **1d**) were obtained. The yields in **1a-d** were 97.0%, 98.2%, 97.9% and 97.5% respectively.

IR: ν , cm⁻¹: 622.86, 719.30, 930.13, 1081.61, 1309.96, 1416.13, 1468.55, 1494.32, 1574.31, 1638.60, 2165.49, 2852.77, 2921.63, 3063.02, 3553.43 for **1a**;

IR: ν , cm⁻¹: 622.49, 722.05, 1084.25, 1377.58, 1464.98, 1573.60, 1636.21, 2163.19, 2853.21, 2922.61, 3340.99 for **1b**;

The IR spectra for **1c** and **1d** was in full agreement with the data presented for compound **1b**.

1a C₂₀H₃₈N₂Cl₂O₄ Calcd.: N 6.35%, Cl 16.10%; found: N 6.36%; Cl 16.09%.

1b C₃₀H₅₈N₂Cl₂O₄ Calcd.: N 4.82%, Cl 12.22%; found: N 4.81%, Cl 12.23%.

1c C₃₈H₇₄N₂Cl₂O₄ Calcd.: N 4.04%, Cl 10.24%; found: N 4.05%, Cl 10.24%.

1d C₄₂H₈₂N₂Cl₂O₄ Calcd.: N 3.74%, Cl 9.48%; found: N 3.75%, Cl 9.49%.

The corrosion experiments

The plates of OL37 steel were polished with 600 mesh emery paper, washed with acetone and dried 24 hours at 150 °C.

The "work" water was prepared as follows: to 900 ml water derived from Arges river sodium tripolyphosphate (0.02g, 20 ppm) and hydrochloric acid until pH = 3-3.5 were added. The reaction mixture was maintained with stirring at room temperature for 20-40 min. A 30 mL aliquot was put in a closed flask and different concentration (4-50 ppm) of pyridinium hydrochlorides **1a-d** was added. Corrosion experiments were carried at room temperature, by the gravimetric method in statical conditions. The OL37 plates were exposed to corrosive acidic medium allowed to stand at room temperature at decided time (1 hour-90 days). After a given time, the plate was take out, washed with acetone, dried 4 hours at 150 °C and weight losses was determined.

Analyses

The NMR spectra have been recorded on a BRUKER AVANCE DRX 400 instrument, equipped with a 5 mm inverse detection multinuclear probehead and field gradients on the z axis, operating at 400 MHz for ¹H and at 100 MHz for ¹³C nuclei. The COSY, HMQC and HMBC spectra have been recorded with standard Bruker parameters in the versions employing pulsed field gradients. All spectra have been recorded in deuterated chloroform, and the chemical shifts

have been reported as δ values referenced to TMS as internal standard. Infrared spectra were run on a BRUKER VERTEX 70 instrument equipped with a Golden Gate diamond ATR.

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Figure 1. Pyridinium hydrochlorides with long alkyl substituents.

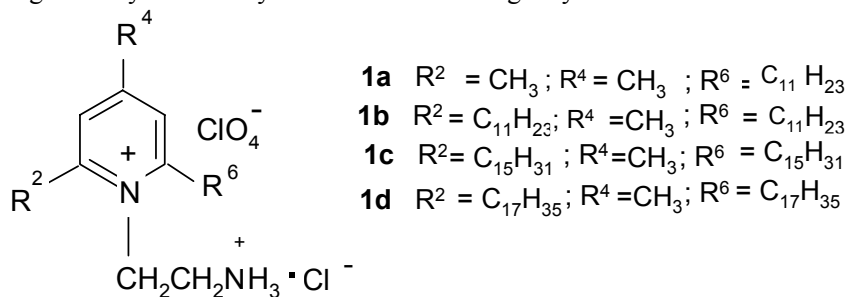


Table 2

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| 6 | Content in SiO_2 | mg/l | 6 |
| 7 | Content in Ca^{2+} | mg/l | 38.1 |
| 8 | Content in Mg^{2+} | mg/l | 10.4 |
| 9 | Content in Na^+ | mg/l | 4.1 |
| 10 | Content in K^+ | mg/l | 0.1 |
| 11 | Content in HCO_3^- | mg/l | 55.4 |
| 12 | Content in Cl^- | mg/l | 8.0 |
| 13 | Content in SO_4^{2-} | mg/l | 8.7 |
| 14 | Content in PO_4^{3-} | mg/l | 0.04 |
| 15 | Conductivity | $\mu\text{s}/\text{cm}$ | 270 |
| 16 | pH_i (initial) | - | 6-6.5 |
| 17 | pH_w (work) | - | 3-3.5 |

