

N-Substituted derivatives of ϵ -caprolactam and their thermal and chemical behavior

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**In memory of C.D. Nenitzescu on the occasion of his 100th birthday
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Abstract

Among several water soluble N-substituted derivatives, N-(β -cyanoethyl)- ϵ -caprolactam was found to be the best solvent for the separation of aromatic hydrocarbons from various gasoline fractions. The products that resulted by the degradation at 150°C of the concentrated aqueous solutions of N-(β -cyanoethyl)- ϵ -caprolactam were studied.

Keywords: ϵ -Caprolactam derivatives, cyanoethylation

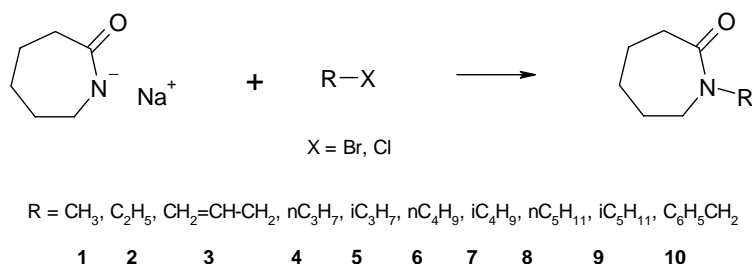
Introduction

ϵ -Caprolactam and its N-methyl derivative were initially recommended for the extraction of aromatic hydrocarbons from reformation and pyrolysis gasoline,^{1,2} but their stability and performance had proven to be unsatisfactory. In order to increase selectivity, small amounts of water are usually added to the water-soluble solvents used for extraction,³ but in this case the thermal and chemical stability of the solvents decreases, due to not entirely known processes.

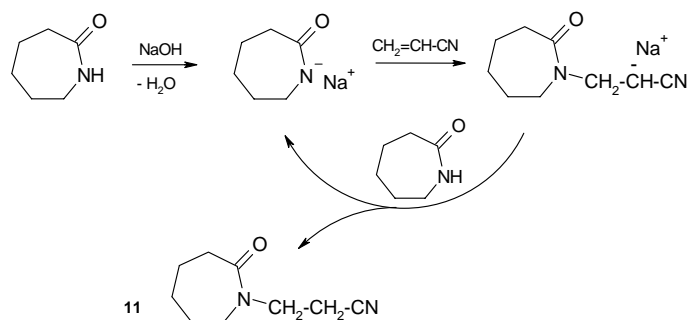
In this paper we present a series of new water-soluble N-substituted derivatives of ϵ -caprolactam that were synthesized and tested as extraction solvents; N-(β -cyanoethyl)- ϵ -caprolactam had proven to be the most efficient, so its thermal and chemical stability was also studied, in order to clarify the nature of the products that result from its decomposition during use.

Results and Discussion

N-Alkylated derivatives of ϵ -caprolactam were prepared by reaction of sodium ϵ -caprolactam with alkyl halides. Best results were obtained when primary halogenated derivatives were used, while the secondary ones gave partial elimination. In all cases small quantities of ϵ -caprolactam oligomers are formed because of its anionic polymerization⁴. Derivatives where R = CH₃, *n*-C₄H₉ were previously also prepared by other methods.^{5, 6}



Unlike alcohols, thiols or amines when both heterogeneous and homogeneous basic catalysts can be used,^{7,8} cyanoethylation of ϵ -caprolactam could be performed only in the presence of quaternary ammonium bases,⁹ using dioxane as a solvent, with a reduced yield (65%) difficult to separate from the unreacted products. We observed that sodium ϵ -caprolactam obtained by reacting ϵ -caprolactam in toluene with the equivalent amount of solid sodium hydroxide by azeotropic distillation of water, was soluble enough in warm toluene so that reduced concentrations such as 0.1% mol could be used as a catalyst for cyanoethylation.



Addition reaction to the acrylonitrile took place easily, even at room temperature, when the anionic product converted continuously new amounts of ϵ -caprolactam into the corresponding sodium compound. At the end, the catalytic system was neutralized with the appropriate amount of acid and the salts and small amounts of oligomers were filtered. After removal of the solvent, N-(β -cyanoethyl)- ϵ -caprolactam **11** with improved yields and high purity was obtained by vacuum distillation.¹⁰

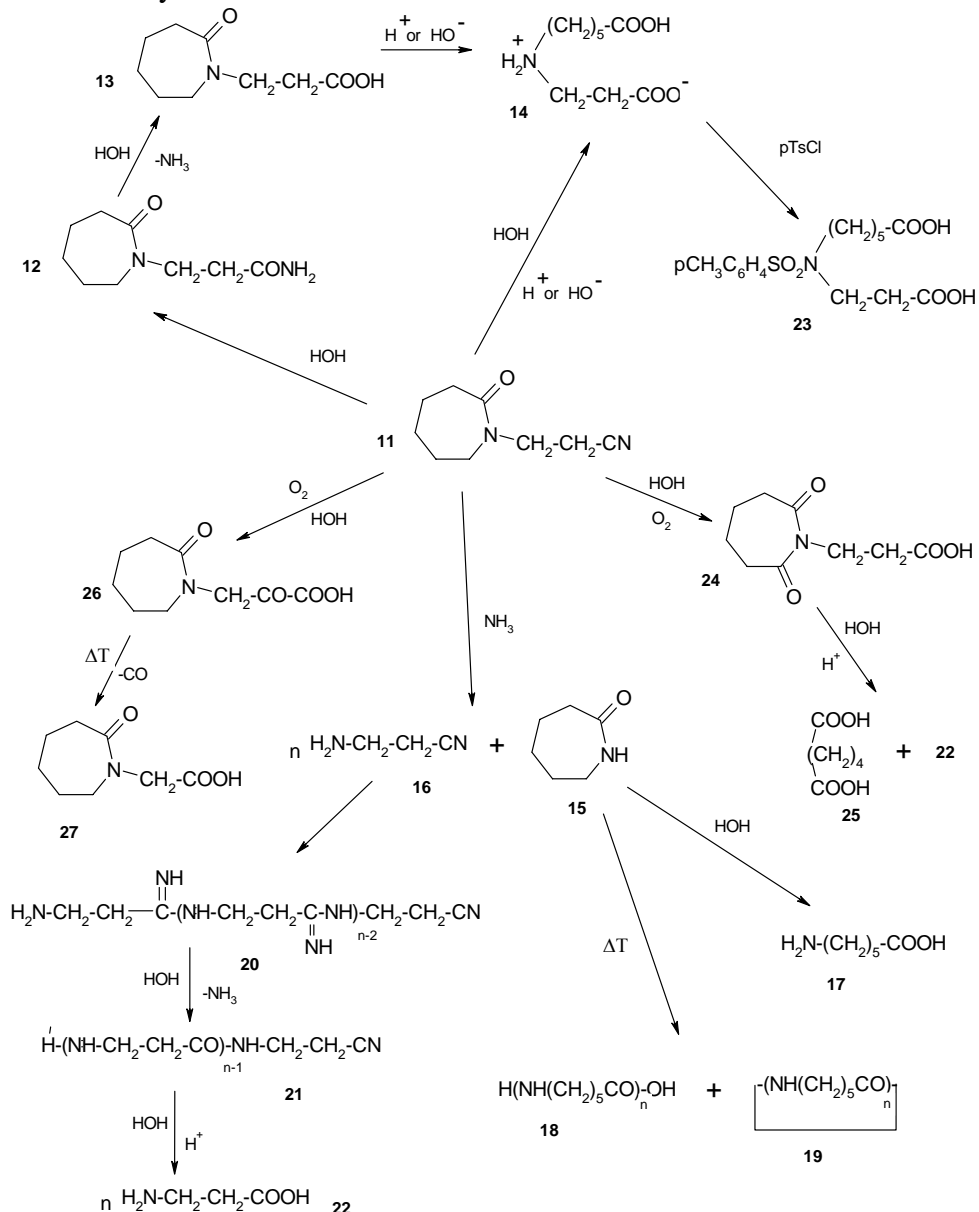
All the ϵ -caprolactam N-alkyl derivatives that were synthesized are neutral and soluble in water and aromatic hydrocarbons, but insoluble in alkanes. In order to assess their relative

selectivity as extraction solvents, coefficients of activity at infinite dilution and the distribution of aromatics comparative to the corresponding alkanes (with the same number of carbon atoms), were determined. Thermogravimetric analysis showed that all products are thermally stable at temperatures up to 250°C and the observed weight loss was due only to the evaporation process. Small amounts of added water (1-10%) increased extraction selectivity for aromatics and improved the separation of the extract. Among the synthesized compounds, N-(β -cyanoethyl)- ϵ -caprolactam proved to be the most powerful and selective solvent, comparable to the industrially used N-methyl-2-pyrrolidone or sulfolane. Because aromatics are industrially separated from the extract by stripping, at temperatures up to 150°C, further studies on the thermal stability of N-(β -cyanoethyl)- ϵ -caprolactam **11** were required. With this purpose compound **11** was heated at 150°C for 1000 h with small amounts of water (2-10%) and its acidic and basic hydrolysis was studied in various conditions. Products formed by normal and oxidative hydrolysis (in the presence of air or other oxidants) were, identified by TLC and GC using our standards especially synthesized for this purpose as it is described in experimental part. Hydrolytic stability of **11** was proved to be much higher than that of ϵ -caprolactam and it was found to be dependent on the concentration of water in the solvent, reaction time and other reaction conditions. It was also found that after 1000 h at 150°C, less than 5% of N-(β -cyanoethyl)- ϵ -caprolactam was degraded. The amount of water in the solvent decreased in time (Karl-Fischer), while small amounts of ammonia evolved all through the process, lowering the rate of degradation; pH varied from neutral to acid (5.5-6) and the acidity indices increased from 0 to 4-5 mg KOH/g. According to the experimental data, the reaction scheme describing the hydrolytic and oxidative degradation of **11** is depicted in **Scheme 1**.

Only the cyano group of N-(β -cyanoethyl)- ϵ -caprolactam **11** was hydrolyzed with small amounts of water at 150°C into the corresponding amide **12**, which by elimination of ammonia turned into acid **13**. N-(β -cyanoethyl)- ϵ -caprolactam **11** was transformed partially into ϵ -caprolactam but no acrylonitrile could be detected. Reduced amounts of ϵ -aminocaproic acid **17** and its linear **18** and cyclic oligomers **19** were separated and could be detected by comparison with authentic samples presented in the literature¹¹. Further ring opening hydrolysis of **13** to the azasebacic acid **14** was more difficult and took place only in the presence of boiling concentrated acids or bases (20%). Due to its amphiphilic structure, **14** could not be N-acylated with acetic anhydride or benzoyl chloride, when **14** partially turned into the β -caprolactampropionic acid **13** and oligomeric condensation products of undetermined structure; **14** could be N-acylated with *p*-toluenesulfonic acid chloride, when sulfonamide **23** was obtained. The presence of β -aminopropionitrile **16** and its polycondensation oligomers **20-21**, that were detected in solution and compared with samples described in the literature¹² was explained by the somehow unexpected¹³ transcyanoethylation of **11**, due to the ammonia resulted from the formation of **13**. β -Aminopropionitrile **16** and equivalent amounts of ϵ -caprolactam **15** were thus formed; **15** partially hydrolysed further on to ϵ -aminocaproic acid **17**, in parallel with the oligomerization to linear **18** and cyclic products **19**. In his turn, β -aminopropionitrile **16** gave the oligomer **20**, which partially hydrolysed further on to the polyamide **21**. β -Alanine **22** was detected too, but

only after acidic hydrolysis. Ammonia that was formed in the hydrolysis of **20** participates also in the transcyanoethylation of **11**.

When degradation of **11** was performed in the presence of air or other oxidants (*i.e.* potassium persulfate), both hydrolysis and oxidation processes took place. Small amounts of α -ketoacid **26** were formed and, by its further decarbonilation, N- ϵ -caprolactamacetic acid **27** was produced. Most probably, **24** was formed too, because traces of adipic acid **25** and β -alanine could also be detected. These oxidative processes did not take place under nitrogen atmosphere or in the absence of any oxidants.



Scheme 1

Hydrolytic and oxidative degradation of N-(β -cyanoethyl)- ϵ -caprolactam **11**.

Experimental Section

General Procedures. IR spectra were recorded on a Specord 71 IR Karl Zeiss Jena spectrophotometer (CCl₄ or KBr disc). GC analyses were performed on a Pye-Unicam 104 chromatograph equipped with a hydrogen flame ionization detector, glass column (1.5m / 4mm) with Chromosorb W 80/100 mesh and methyl silicon SE30 (10%), using nitrogen as a carrier gas. A MOM equipment was used for DTA measurements. Kieselgel G plates and BuOH : HCOOH : H₂O (75 : 15 : 10) as solvent were used for TLC; iodine 1% and ninhydrine 0.5% were used as visualization reagents. The observed R_f values for the main components are as follows: **11** (0.65), **12** (0.73), **13** (0.50), **14** (0.38), **16** (0.25), **17** (0.44), **22** (0.32), **24** (0.51), **25** (0.79), **27** (0.63).

Thermal degradation of N-(β-cyanoethyl)-ε-caprolactam **11** was performed by heating it at 150°C for 1000h in a stainless steel autoclave with 5% added water, either under nitrogen, in the air or in the presence of oxidants (potassium persulfate 10%, buffered solution). Properties such as pH, acidity index (mg KOH / g), refractive index and chemical composition were monitored in all cases. At the end the reaction mixture was cooled, diluted with cold water (3 vol.) and filtered. The separated white gel (0.5% of starting material **11** - after drying on P₂O₅) was soluble only in formic and acetic acids and partially soluble in HCl 25% (β-alanine oligomers – **21** slight IR absorption –CN at 2260 cm⁻¹); the insoluble part (ε-caprolactam oligomers - **18**, **19**) dissolved only after a long hydrolysis time, when ε-aminocaproic acid **17** was formed.

The aqueous filtrate was passed onto a strongly acidic ion exchanger column (Zerolith 225) and by eluting with water, **11** and ε-caprolactam **15** were separated. By eluting with NH₃ (2%), linear oligomers **18**, β-alanine oligomers **21**, β-aminopropionitrile **16** and ε-aminocaproic acid **17** were obtained. By further eluting with NaOH (4%), **17** and acids **13**, **27** and **26** (which gave a precipitate with 2,4-dinitrophenylhydrazine), together with **14** and traces of the other previously mentioned products were washed out from the column.

General procedure for the alkylation of ε-caprolactam with alkyl halides

In a three-neck flask equipped with dropping funnel, stirrer and condenser with CaCl₂ tube, sodium was dispersed in a small volume of dry xylene, under reflux. A solution of ε-caprolactam in dry xylene was then added dropwise and the reaction mixture was refluxed continuously until all sodium was reacted, when a 0.5M solution of sodium ε-caprolactam in xylene was thus obtained. The reaction mixture was then cooled below the boiling point of the alkylating reagent and a small excess of alkyl halide was added portionwise under stirring. The cooled reaction mixture was filtered, xylene was removed under vacuum and the product was then distilled. For the C₃-C₅ derivatives, the unreacted ε-caprolactam could be removed by extracting the xylenic solution with water.

N-Methylcaprolactam (1). obtained by bubbling methyl bromide in the reaction flask; $\eta = 51\%$, b.p. 90.5-94°C / 4-5torr, $d_4^{25} = 1.1070$, $n_D^{25} = 1.4800$ (lit.⁹ $n_D^{25} = 1.4818$); for $C_7H_{13}NO$, calculated: C, 66.10; H, 10.30; N, 11.01%; found: C, 65.8; H, 10.5; N, 10.7%; $\nu_{\max}(\text{cm}^{-1})$ 2920 (CH_2 as), 2850 (CH_2 sim), 1650 ($\text{C}=\text{O}$).

N-Ethylcaprolactam (2). from ethyl bromide; $\eta = 50\%$, b.p. 95-113°C / 3-4torr, $d_4^{25} = 0.9837$, $n_D^{25} = 1.4729$ (lit.⁹ $n_D^{25} = 1.4777$); for $C_8H_{15}NO$, calculated: C, 68.04; H, 10.70; N, 9.92%; found: C, 65.9; H, 10.5; N, 10.3%; $\nu_{\max}(\text{cm}^{-1})$ 2940 (CH_2 as), 2870 (CH_2 sim), 1650 ($\text{C}=\text{O}$).

N-Allylcaprolactam (3). from allyl chloride; $\eta = 70.5\%$, b.p. 125-131°C / 10torr, $d_4^{25} = 0.9894$, $n_D^{25} = 1.4888$; for $C_9H_{15}NO$, calculated: C, 70.55; H, 9.86; N, 9.14%; found: C, 68.30; H, 9.7; N, 9.3%; $\nu_{\max}(\text{cm}^{-1})$ 3080 (substituted ethylene).

N-Propylcaprolactam (4). from *n*-propyl bromide; $\eta = 62\%$, b.p. 100-125°C / 3-5torr, $n_D^{25} = 1.4739$; or by catalytic reduction (Pd/C) of **3** in MeOH, $\eta = 84\%$, b.p. 98-103°C / 4torr, $d_4^{25} = 0.9693$, $n_D^{25} = 1.4751$; for $C_9H_{17}NO$, calculated: C, 69.63; H, 11.03; N, 9.02%; found: C, 69.9; H, 10.7; N, 9.1%; $\nu_{\max}(\text{cm}^{-1})$ 2920 (CH_2 as), 2850 (CH_2 sim), 1650 ($\text{C}=\text{O}$).

N-Isopropylcaprolactam (5). from isopropyl bromide; $\eta = 18.6\%$, b.p. 91-95°C / 4torr; $d_4^{25} = 0.9809$, $n_D^{25} = 1.4761$; $\nu_{\max}(\text{cm}^{-1})$ 2970 (CH_3 as), 2920 (CH_2 as), 2870 (CH_2 sim), 1650 ($\text{C}=\text{O}$).

N-Butylcaprolactam (6). from *n*-butyl bromide; $\eta = 72\%$, b.p. 82-105°C / 3-5torr, $d_4^{25} = 0.9640$, $n_D^{25} = 1.4731$; for $C_{10}H_{19}NO$, calculated: C, 70.95; H, 11.31; N, 8.27%; found: C, 69.7; H, 11.6; N, 8.4%; $\nu_{\max}(\text{cm}^{-1})$ 2940 (CH_2 as), 2870 (CH_2 sim), 1650 ($\text{C}=\text{O}$).

N-Isobutylcaprolactam (7). from isobutyl bromide; $\eta = 31\%$, b.p. 101-104°C / 4-5torr, $d_4^{25} = 0.9438$, $n_D^{25} = 1.4715$; for $C_{10}H_{19}NO$, calculated: C, 70.95; H, 11.31; N, 8.27%; found: C, 69.7; H, 11.6; N, 8.0%; $\nu_{\max}(\text{cm}^{-1})$ 2920 (CH_2 as), 2835 (CH_2 sim), 1650 ($\text{C}=\text{O}$).

N-Amylcaprolactam (8). from amyl bromide; $\eta = 66\%$, b.p. 158-160°C / 10torr, $d_4^{25} = 0.9292$, $n_D^{25} = 1.4722$; $\nu_{\max}(\text{cm}^{-1})$ 2920 (CH_2 as), 2850 (CH_2 sim), 1645 ($\text{C}=\text{O}$).

N-Isoamylcaprolactam (9). from isoamyl bromide; $\eta = 63.5\%$, b.p. 105-113°C / 4-5torr, $d_4^{25} = 0.9347$, $n_D^{25} = 1.4711$; for $C_{11}H_{21}NO$, calculated: C, 72.08; H, 11.54; N, 7.64%; found: C, 68.3; H, 11.7; N, 8.3%; $\nu_{\max}(\text{cm}^{-1})$ 2930 (CH_2 as), 2860 (CH_2 sim), 1645 ($\text{C}=\text{O}$).

N-Benzylcaprolactam (10). from benzyl chloride; $\eta = 75\%$, b.p. 176-182°C / 3torr; m.p. 60-61°C; for $C_{13}H_{17}NO$, calculated: C, 76.81; H, 8.42; N, 6.89%; found: C, 76.1; H, 8.6; N, 7.0%; $\nu_{\max}(\text{cm}^{-1})$ 3060 (CH arom), 3025 (CH_2); λ_{\max} (nm, H_2O , 10^{-5}M) 260.

N-(β -Cyanoethyl)- ϵ -caprolactam and its degradation products

N-(β -Cyanoethyl)- ϵ -caprolactam (11). In a three-neck flask equipped with a Dean Stark trap, dropping funnel, mechanical stirrer and condenser with CaCl_2 tube, ϵ -caprolactam (56.5g, 0.5mol) was dissolved in warm toluene (140mL, $\sim 60^\circ\text{C}$). Solid NaOH (0.2g, 0.005mol) was then introduced under stirring and the mixture was refluxed until no more water separated in the Dean Stark tube ($\sim 0.1\text{mL}$). After cooling at 15°C , acrylonitrile (33.8mL, 27.2g, 0.5mol) was added dropwise under stirring and the reaction mixture was heated to 50°C for 1h, cooled and neutralized with conc. sulfuric acid (phenolphthalein). After filtration, toluene and the unreacted acrylonitrile were removed under vacuum and the residue was distilled to obtain colourless

crystals of *N*-(β -cyanoethyl)- ϵ -caprolactam (80g, η = 95%), m.p. 35.5-36°C; d_4^{25} = 1.0720, n_D^{25} = 1.4930 (lit.⁹ m.p. 32-34°C, d_4^{25} = 1.0740, n_D^{25} = 1.4903); for $C_9H_{14}N_2O$, calculated: C, 65.03; H, 8.49; N, 16.85%; found: C, 65.1; H, 8.46; N, 17.1%; $\nu_{max}(cm^{-1})$ 2944 (CH_2 as), 2860 (CH_2 sim), 2260 ($C\equiv N$), 1665 ($C=O$). The product was slightly hygroscopic and soluble in water and most of organic solvents, but not in alkanes. Basicity (as pK_a of the cation BH^+) is -2.23 in acetic acid (close to formamide, -2.45, but smaller than ϵ -caprolactam, -1.52) and 3.39 in water (ϵ -caprolactam 0.43), all values determined in equivalent conditions.¹⁴ Its dipole moment is 4.36D and studies in benzene solution suggest an antiparallel molecular association.¹⁵ The measured dielectric constant was 40.3 at 25°C and 27.4 at 90°C.

***N*- ϵ -Caprolactampropionamide (12).** *N*-(β -cyanoethyl)- ϵ -caprolactam **11** (6.6g, 58.4mmol) was added portionwise to concentrated sulfuric acid (8.5mL, 15.2g, 155mmol). The mixture was diluted with ice water (150mL), brought to pH 3-3.5 with $Ca(OH)_2$ and filtered while still hot (70°C). The solution was then brought to pH 6-6.5 with $Ba(OH)_2$, filtered and concentrated, when amide **12** separated and was recrystallized from benzene to give white crystals (η = 85%), m.p. 144.5°C, soluble in water and insoluble in aromatic and chlorinated hydrocarbons; for $C_9H_{16}N_2O_2$, calculated: C, 58.67; H, 8.75; N, 15.21%; found: C, 59.0; H, 8.8; N, 15.5%; $\nu_{max}(cm^{-1})$ 3320 (NH as asoc.), 3170 (NH sim asoc.), 1690 ($C=O$ amide), 1620 ($C=O$ lactame).

***N*-(β - ϵ -Caprolactam)propionic acid (13).** *N*-(β -cyanoethyl)- ϵ -caprolactam **11** (3g, 26.5mmol) was refluxed for 10h in aqueous NaOH (5%, 45mL), then the reaction mixture was diluted with water (100mL) and passed onto a column of Zerolith 225. Fraction with pH 5.5-2.5 was collected and concentrated in vacuum. The solid was recrystallized from carbon tetrachloride to give **13** as white crystals (5.37g; η = 97%), m.p. 95.3-96.8°C, soluble in water, alcohol, aromatic and chlorinated hydrocarbons; acidity index 299mgKOH/g (calculated 302.9), k_a = 2.51×10^{-5} ; for $C_9H_{15}NO_3$, calculated: C, 58.36; H, 8.16; N, 7.56%; found: C, 58.6; H, 8.2; N, 7.4%; $\nu_{max}(cm^{-1})$ 2920 (CH_2 as), 2840 (CH_2 sim), 2700-2500 (OH asoc.), 1599 ($C=O$).

4-Azasebacic acid (14). *N*-(β -cyanoethyl)- ϵ -caprolactam **11** (5g, 44.2mmol) was refluxed for 20h in aqueous NaOH (20%, 45mL), then the reaction mixture was diluted with water (50mL) and passed onto a column of Zerolith 225. After washing with water, the column was eluted with aqueous NH_3 (2%) and the fraction with pH \leq 6.5 was collected and concentrated in vacuum. The solid residue was recrystallized from ethanol to give **14** (5.6g; η = 92%), m.p. 179-180.5°C, soluble in water, k_a = 2.05×10^{-5} ; for $C_9H_{17}NO_4$, calculated: C, 53.19; H, 8.43; N, 6.89%; found: C, 54.0; H, 8.6; N, 6.8%; $\nu_{max}(cm^{-1}, KBr)$ 3200-3020 (NH_2^+ as and OH), 2555-2400 (NH_2^+ sim), 1695 (COOH), 1550 (COO^- asim), 1405 (COO^- sim). **14** was also prepared by acidic hydrolysis of **11**, with HCl (25%) for 60h, η = 57%.

***N*-(*p*-Toluensulfonamido)-4-azasebacic acid (23).** To a solution of 4-azasebacic acid **14** (0.5g, 2.5mmol) in water (2mL) *p*-toluensulfonic acid chloride (0.8g, 4.2mmol) was added and the pH was brought to 9-10 with aqueous NaOH (10%). The mixture was stirred continuously and pH was maintained to 8.5-9 (with aqueous NaOH solution) until it remained stationary (after about 7h). The unreacted acid chloride was extracted with diethyl ether (5mL) and the aqueous layer was made acidic with HCl (10%) and the precipitate was filtered and recrystallized from

benzene to give **23** (0.8g, $\eta = 77\%$), m.p. 105.3-106.5°C; acidity index 313.78mgKOH/g (calculated 318.93), $k_{a1} = 5.54 \times 10^{-5}$; $k_{a2} = 1.31 \times 10^{-5}$ $\nu_{\max}(\text{cm}^{-1})$ 3100 (CH arom.), 2900 (CH₂ asim), 2840 (CH₂ sim), 2900-2400 (OH asoc.), 1695 (COOH), 1320 (SO₂ asim), 1140 (SO₂sim). ***N*- ϵ -Caprolactamacetic acid (27)**. A solution of methyl *N*- ϵ -caprolactamacetate (3.4g, 18.3mmol) in alcoholic KOH (30.5mmol; 90mL) was stirred overnight and then neutralized with HCl (phenolphthalein). The alcohol was removed and the residue was dissolved in water (25mL) and extracted with diethyl ether (5x5mL). The aqueous layer was made acidic with HCl (Congo red) and evaporated. The residue was then extracted with acetone (20mL), the insoluble salt (KCl) was filtered and the solution was concentrated to obtain **27** as crystals with m.p. 144-145°C, soluble in water, ethanol, acetone and chloroform, insoluble in benzene and CCl₄, acidity index 327.17mgKOH/g (calculated 327.74), $k_a = 2.82 \times 10^{-4}$; $\nu_{\max}(\text{cm}^{-1})$ 3200-2500 (OH asoc.), 1770 (COOH monom.), 1730 (COOH dimer), 1645 (C=O).

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