SYNTHESIS AND CHARACTERIZATION OF *BIS*- AND *TRIS*-(4-CARBOXYBENZOYL)-ALKANEAMINES

L. GUARDA[†], N. PARRA[†], M. S. CHÁVEZ[†], J. BELMAR[†], C. A. JIMÉNEZ[†], J. PASÁN[‡], C. RUIZ-PÉREZ[‡]*

[†]Department of Organic Chemistry, Faculty of Chemical Sciences, University of Concepcion, Casilla 160-C, Concepción, Chile.
[‡]Laboratorio de Rayos X y Materiales Moleculares. Departamento de Física Fundamental II. Facultad de Física. Universidad de La Laguna. Avda. Astrofísico Francisco Sánchez s/n, E-38204 La Laguna. Spain
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ABSTRACT

A practical and efficient protocol to obtain *bis*- and *tris*-(4-carboxybenzoyl)alkaneamines based on monoprotected 1,4-benzenedicarboxylic acid is reported here. *N*-(4-methoxycarbonylbenzoyloxy)succinimide was treated with aliphatic diamines and triamines to form aliphatic hydrocarbon-linked *bis*- and *tris*-amides ***4a–4e***. The yields ranged from good to very good and showed that choosing the right acylating agent is a key point in this synthesis. All the compounds were characterized by elemental analysis, FTIR, and ^{1}H NMR.

Keywords: *Acylating Agents, Ligands design, Amides.*

INTRODUCTION

Coordination compounds with infinite one-, two-, and three-dimensional network structures have been intensively studied. Particularly compounds with backbones constructed by metal ions as "nodes" and divergent polytopic organic ligands as "linkers", form a great family of polymers; which are called "coordination polymers" (CPs).[1] These kinds of materials have been studied in ionic exchange,[2] separation,[3] chemisorption,[4] gas storage,[5] catalysis,[6] magnetism,[7] optoelectronic[8] and luminescence.[9] In the design and construction of CPs the size, shape and functionalities in the connectors have become an extremely important factor, because of the particular properties that they give to the final material.[10] The connectors in CPs can be separated in two big families, rigid and flexible ligands. Compared with the rigid ligand, using flexible ones to construct CPs is more difficult and developing systematic methodologies to synthesize from *prior* designed structure for these systems is still a great challenge. The most important advantage in final structures based on flexible ligands is the sensitivity to many subtle factors. Flexible ligands can adopt different conformations as a consequence of free rotations about their single bonds, giving raise to low symmetry structures.[11] On the other hand, the "breathing" ability and adaptative recognitions properties can be achieved using the flexibility as a feature in the design of new connectors.[12] Developing of CPs based on flexible ligands is a good opportunity to get a better insight into the details of a self-assembly process and it is a way for raising some signposts toward future research on predicted and pre-designed CPs.

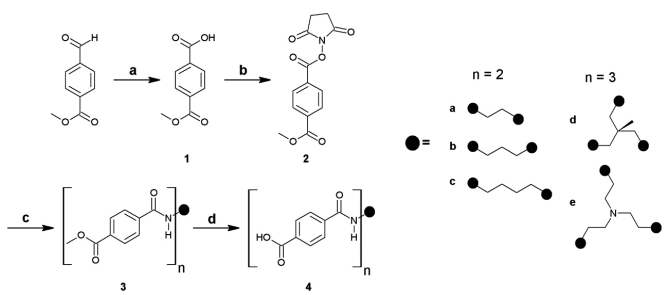
Polytopic linkers such as carboxylate have allowed the synthesis of rigid structures which do not collapse easily and can exhibit permanent porosity. In addition, they are neutral networks that prevent counterion inclusion in CPs.[13] On the other hand, the amide group has been described to be an important synthon, both in organic crystals[14] and coordination polymers.[15] Although the amide groups can also act like binding sites,[16] their affinities towards the metallic centers are much lower. In the synthesis of coordination polymers and organic crystals, the amide groups have been involved in increasing the stability through hydrogen bond interactions, being this, the most important contribution to the supramolecular structures.[17] In spite of the restricted rotation around C-N amide bond, there is some flexibility associated to it. This restricted rotation feature allows to be defined as a "weak point" (non-rigid area), important in the solid to allow the breathing modes.[18] The rational synthetic design of a connector that integrates these important features should be kept in mind in the process of developing new coordination polymers.

Our goal is to obtain ligands that combine these characteristics. *N*-hydroxysuccinimide esters have been used to obtain *bis*- and *tris*-amides. We described the synthesis of *N,N* – disubstituted - 3,5 – *di* – *tert* – butyl – 2 – hydroxyl - benzamides using the corresponding ester, some years ago.[19] This procedure has resulted to be the best choice to synthesize amides, even better than the obvious method using the chloride derivative of the acid and the corresponding diamine. These esters are acylating agents which can be used under very mild conditions, usually providing good yields. To our knowledge, *bis*- and *tris*-(4-carboxybenzoyl)alkaneamines have never been described by other authors before.

RESULT AND DISCUSSION

The Scheme 1 shows the synthetic route followed to the preparation of the corresponding *bis*-amides. In the first place, the monomethyl ester of the 1,4-benzenedicarboxylic acid (**1**) is obtained in an almost quantitative yield by an oxidation of methyl 4-formylbenzoate in acidic media, the temperature must be carefully controlled to avoid the ester hydrolysis. The succinimide ester **2** is also easily obtained and readily crystallized. Since **2** is a fairly stable compound, it can be stored and used whenever needed. Then, the *bis*-amides **3a-e** and **4a-e** due to their high insolubility in water, can be easily purified by successive washing. The physical characteristics and the analytical data that confirm the compound structures are presented in the Experimental section.

The infrared spectra for **4a-e** show a broad absorption from 3000 to 2500 cm^{-1} characteristic for acid OH stretching. A sharp absorption band close to 3300 cm^{-1} for NH stretching. Two C=O absorption are shown for **3a-e**, one of them is shifted to lower wavenumber for **4a-e**, that account for the ester-acid transformation. The ^{1}H NMR spectra show two important low field signals, the first, between 14 and 13 ppm for OH (2H), the second, below 9 ppm for NH (2H).



Scheme 1. (a) $KMnO_4$, H_2SO_4, H_2O, 10°C, 2 h (b) *N*-Hydroxysuccinimide, DCC, 10°C, dioxane, 24 h, r.t. (c) di- or triamine, Et_3N, DMF, DMPA, 12 h, r.t. (d) KOH, MeOH/H_2O, 3 h, reflux.

The NH signal is broad, but it is possible to observe the multiplicity associated with the coupling with methylene of the alkyl chain. Signals corresponding to the aromatic hydrogens can be identified without any doubt, because they constitute an AA'BB' spin system that gives rise to a doublet of doublets centered close to 8.00 ppm in all cases (Figure 1).

The high field signals are characteristics to each compound depending on the nature of the aliphatic chain. In the case of **4a** (Figure 1), it is possible to observe one signal that integrates by four hydrogens and presents a diffuse multiplicity associated to NH to 8.79 ppm. The melting points, as expected for amides, are high.

e-mail: cjimenez@udec.cl

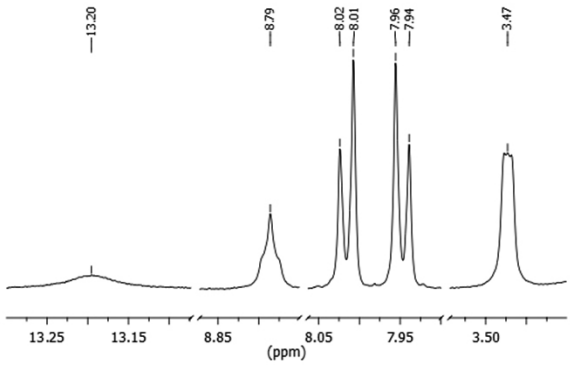
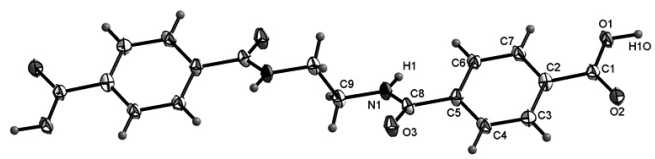
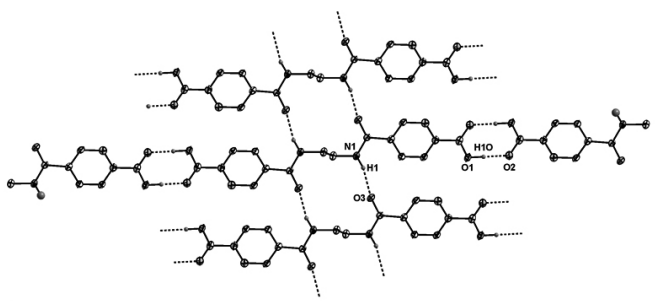


Figure 1. Selected areas of ^{1}H-NMR of compounds **4a**.

In order to examine the molecular structure of these connectors, as well as the organization in the solid state, attempts to obtain single crystals were carried out. By slow evaporation of dimethylsulphoxide solution, crystals suitable for X-ray diffraction were obtained for **4a** and **4e.** Pertinent crystallographic details were given in the Table 1. The crystal structures of **4a** and **4e** are different and because of this they will be described separately. The asymmetric unit for **4a** contains half of the molecule, since it sits on an inversion center and the alkyl chains exhibit a staggered conformation (Figure 2a). The molecules of **4a** are engaged in amide-to-amide hydrogen bonds (N-H•••O) which propagate in the form of a *b*-sheet network along the *a* axis. Alongside, the benzoic acid groups are linked via a double O-H•••O hydrogen bond in the classic synthon for carboxylic acids along the [02-1] direction to build a supramolecular two-dimensional network. (Figure 2b). The relevant parameters of the hydrogen bonds discussed in the text are given in Table 2.



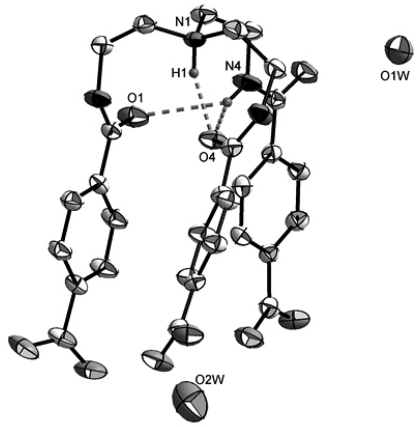
a



b

Figure 2. a) View of **4a** molecule with numering scheme, **b)** Packing diagram showing the β-sheet network and dimeric synthon for carboxylic acid. H atoms not involved in hydrogen bond have been omitted.

The asymmetric unit in **4e** contains three molecules, one *tris*-amide molecule and two crystallization water molecules. The *tris*-amide is found in its zwitterion form, with the amine nitrogen protonated and one carboxylate arm deprotonated. Although the three amidobenzoic groups are free to rotate in solution; remarkably, in the solid state they are bent to the same direction to give the molecule a pseudo-calix form (Figure 3a). This calix conformation is supported by intramolecular N-H•••O interaction (Table 2). Each molecule is connected to two adjacent *tris*-amide molecules through O-H•••O hydrogen bonds. The carboxylic moieties act as single hydrogen bond donors, but the carboxylate moiety acts as a double acceptor of hydrogen bond (Figure 3b). Additionally, each unit is further linked through π•••π interaction and hydrogen bond involving the water molecules.



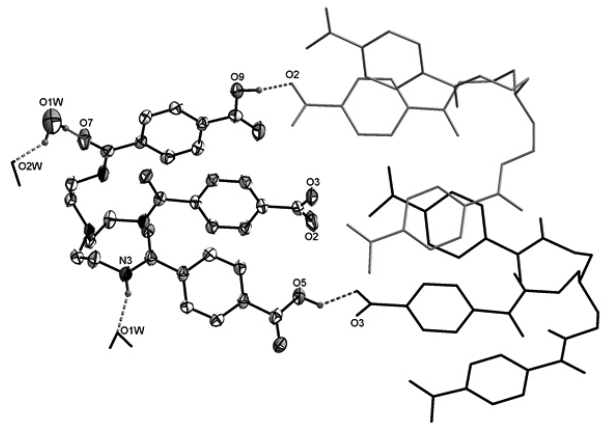


Figure 3. a) View of pseudo-calix conformation for **4e**. Intermolecular hydrogen bonds are drawn as grey broken lines. **b)** Perspective view of hydrogen bonded **4e** interactions. H atoms not involved in hydrogen bond and O2W interactions have been omitted for clarity.

Table 1. Crystallographic data for **4a** and **4e**.

	4a	**4e**
Formula	$C_{18}H_{16}N_2O_6$	$C_{36}H_{32}N_6O_{16}$
F.W.	356.33	626.61
Crystal System	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
a (Å)	4.9952(10)	11.3070(8)
b (Å)	5.0381(12)	13.8360(11)
c (Å)	16.148(3)	18.9020(17)
a (deg)	98.371(3)	-
b (deg)	96.288(4)	101.582(7)
g (deg)	90.592(3)	-
V (Å^3)	399.49(15)	2896.9(4)
Z	1	4
m (mm^{-1})	0.113	0.111
r_{cal} (g cm^{-3})	1.481	1.437
R1 (I>2s(I))	0.1118	0.0596
wR2 (on F^2 all data)	0.3752	0.1275

Table 2. Relevant Hydrogen Bond Parameters in **4a**/**4e**.

Comp.	type[a]	H•••A (Å)	D•••A (Å)	D-H•••A (°)
4a	N(1)-H•••O(3[a])	2.08(4)	2.873(7)	152(1)
	O(1)-H•••O(2[b])	1.63(4)	2.614(7)	173(3)
4e	N(1)-H•••O(4)	1.89(2)	2.751(2)	157(1)
	N(3)-H•••O(1w[c])	2.06(2)	2.860(3)	154(1)
	N(4)-H•••O(4)	2.37(3)	3.094(3)	141(1)
	N(4)-H•••O(1)	2.57(3)	3.242(3)	136(1)
	O(5)-H•••O(3[d])	1.60(3)	2.555(2)	172(3)
	O(9)-H•••O(2[e])	1.60(3)	2.581(3)	169(3)
	O(1w)-H•••O(7)	1.82(3)	2.799(3)	170(2)
	O(1w)-H•••O(2w[f])	1.90(3)	2.777(4)	144(3)
	O(2w)-H•••O(3)	2.07(2)	3.067(4)	170(2)

Symmetry operators: (a) = *x*-1, *y*, *z*; (b) = -*x*, -*y*-1, -*z*+1; (c) = *x*, -*y*+½, *z*+½; (d) = -*x*+2, -*y*, -*z*+1; (e) = -*x*+2, *y*+½, -*z*+½; (f) = *x*-1, -*y*+½, *z*-½.

CONCLUSIONS

We have described a convenient procedure to obtain di- and tricarboxilic linkers. According to our experience, the coupling reaction using *N*-hydroxysuccinimide ester remains as the most efficient procedure to carry out the synthesis of *bis*- and *tris*-amides in good yields (65%).

The new ligands herein reported combine: (a) carboxylate coordination moieties, (b) carboxamide thermal stable groups, and (c) aliphatic flexible chains. These features are attractive to be incorporated in the construction of coordination polymers.

The crystal structures have been determined in two cases, showing the remarkably calix conformation of **4e**. More research is currently carried out to obtain new crystalline coordination polymers.

EXPERIMENTAL

Crystal Structure Determination

The crystallographic data collection of **4a** was carried out in the BM16 beamline of the ESRF (Grenoble, France) with λ = 0.7385 Å at 100(2) K with a CCD detector (ADSCq210r) making phi (φ) scans of one degree per frame. Two orientations of the crystal were measured in order to achieve the desired data completeness. Data were indexed, integrated and scaled using the HKL2000 program.[20] The X-ray data collection of **4e** was performed on a Bruker-Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Orientation matrix and lattice parameters were obtained by least-squares refinement of the reflections obtained by θ-χ scan (Dirax/lsq method). Data collection and data reduction were carried out with the COLLECT[21] y EVALCCD[22] programs. The indexes of data collection were $-6 \le h \le 6$, $-6 \le k \le 6$ and $-20 \le l \le 20$ for **4a**, and $-14 \le h \le 14$, $-16 \le k \le 17$ and $-24 \le l \le 19$ for **4e**. Of the 1660 (**4a**) and 6048 (**4e**) measured independent reflections 1583 (**4a**), and 1889 (**4e**) have $I \ge 2\sigma(I)$. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS-97 and SHELXL-97 programs.[23] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set on geometrical positions except those of the carboxylic groups and the water molecules. All of them were refined with a riding model except those of the carboxylic groups. The final Fourier-difference maps showed maximum and minimum height peaks of 0.524 and -0.480 eÅ^{-3} (**4a**), and, 0.217 and -0.206 eÅ^{-3} (**4e**). The final geometrical calculations and the graphical manipulation were carried out with PARST97[24] and DIAMOND[25] and MERCURY[26] programs, respectively. Crystallographic data (excluding structure factors) for the compounds **4a** and **4e** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 876558 (**4a**) and 876559 (**4e**).

Synthetic Characterizations

All chemicals were obtained from commercial sources. Compounds were characterized by FTIR (Nicolet, Magna 550) KBr discs and ^{1}H NMR (BrukerBioSpinGmbH 400 MHz) using TMS as internal standard. The solvent was DMSO-d_6, except when otherwise stated. Melting points were obtained on a Kofler microscope and are uncorrected. Elemental analyses were obtained in a FISON EA 1108 Analyzer. Chemical shifts for NMR spectra (δ) are quoted in ppm. Infrared values (ν) are quoted in reciprocal centimeters (cm^{-1}).

Synthesis of Bis- and Tris-(4-carboxybenzoyl)alkaneamines.

*Synthesis of 4-(methoxycarbonyl)benzoic acid. **(1)***

In a 500 ml three-necked round-bottomed flask methyl 4-formylbenzoate (15.0 g, 0.091mol) were suspended in 150 ml of water and 10 ml of concentrated H_2SO_4. The mixture was cooled to 10°C and $KMnO_4$ (10.3 g, 0.065mol) was slowly added. The reaction mixture was stirred for 2 h at the same temperature. Then $NaHSO_3$(s) was added until the MnO_2 was fully reduced. The white solid resulting was filtered and recrystallized from ethanol. Yield: 61%; M. P: 222-224°C. **Anal. Elem.** $C_9H_8O_4$: Calcd. C, 60.0; H, 4.5. Found. C, 59.8; H, 4.6. **^{1}H-NMR**: 8.82 (s, 1H, OH), 8.03 (*d*, 2H, H_{ar}, J= 8.3Hz), 7.96 (*d*, 2H, H_{ar} J=8.4Hz), 3.87 (*s*, 3H, OCH_3). FTIR: 3300-2500(OH), 2959(C_{sp2}-H), 2816(C_{sp3}-H), 1700(C=O ester), 1689(C=O acid.), 1570(C=C).

*Synthesis of N-(4-methoxycarbonylbenzoyloxy)succinimide. **(2)***

4-(Methoxycarbonyl)benzoic acid (**1**) (5.3 g, 0.029 mol) and *N*-hydroxysuccinimide (3.7 g, 0.032 mol) were dissolved in 100 ml of dry dioxane. The solution was cooled to 10°C and dicyclohexylcarbodiimide (5.7 g, 0.028 mol) dissolved in 80 ml of the same solvent, was slowly dropped. The reaction mixture was stirred for 24 h at room temperature. The urea was separated by filtration and the filtrate evaporated to dryness. The white solid was recrystallized from ethanol. Yield: 62%, M.P.: 175-177ºC. **Anal. Elem.** $C_{13}H_{11}NO_6$: Calcd. C, 56.3; H, 4.0; N, 5.1. Found. C, 56.2; H, 3.8; N, 5.2. **^{1}H NMR:** 8.24 (*d*, 2H, H_{ar} J=7.2Hz), 8.21 (*d*, 2H, H_{ar} J=8.4), 3.93 (*s*, 3H, OCH_3), 2.92 (*s*, 4H). **FTIR**: 1780(C=O), 1734(C=O).

*Synthesis of N,N`-bis-(4-methoxycarbonylbenzoyl) alkaneamines **(3a-e)**. General Procedure.*

To a solution of *N*-(4-methoxycarbonylbenzoyloxy) succinimide (**2**) (1.0 g, 3.61 mmol) and the corresponding diamine or triamine (1.81 or 1.2 mmol) in 15 ml of DMF, 5 ml of Et_3N and a catalytic amount of DMPA were added. The reaction mixture was stirred for 12 h at room temperature and then poured into ice/10% HCl. The solid was filtered and washed with water and then diethyl ether.

*N,N`-bis-(4-methoxycarbonylbenzoyl)-1,2-ethanediamine. **(3a)**.* Yield: 93%. M.P.: 309ºC. **Anal. Elem.** $C_{20}H_{20}N_2O_6$: Calcd. C, 62.5; H, 5.2; N, 7.3. Found. C, 62.1; H, 4.8; N, 7.2. **^{1}H NMR**: 8.83 (*s*, 2H, NH), 8.03 (*d*, 4H, H_{ar} J=6.0Hz), 7.97 (*d*, 4H, H_{ar}, J=6.0Hz), 3.87 (*s*, 6H, OCH_3), 3.47 ($_s$, 4H). **FTIR**: 3298(NH), 3076(C_{sp2}-H), 2953(C_{sp3}-H), 1723(C=O ester), 1637(C=O amide), 1548 (C=C).

*N,N`-bis-(4-methoxycarbonylbenzoyl)-1,3-propanediamine. **(3b)**.*Yield: 87%. M.P.: >330°C. **Anal. Elem.** $C_{21}H_{22}N_2O_6$: Calcd. C, 63.3; H, 5.6; N, 7.0. Found. C, 63.2; H, 5.2; N, 6.9. **^{1}H NMR**: 9.04 (*t*, 2H, NH, J=8.0Hz), 7.96 (*d*, 4H, H_{ar}, J=13.2Hz), 7.88 (*d*, 4H, H_{ar}, J=13.6 Hz), 3.88 (*s*, 6H, OCH_3), 3.74 (*c*, 4H), 3.55 (*q*, 2H). **FTIR**: 3302(NH), 3072(C_{sp2}-H), 2958(C_{sp3}-H), 1723(C=O ester), 1637(C=O amide), 1544(C=C).

*N,N`-bis-(4-methoxycarbonylbenzoyl)-1,4-butanediamine. **(3c)**.* Yield: 99%. M.P.: >330ºC. **Anal. Elem.** $C_{22}H_{24}N_2O_6$: Calcd. C, 64.1; H, 5.9; N, 6.8. Found. C, 63.9; H, 5.6; N, 6.8. **^{1}H NMR**: 8.24 (*d*, 4H, H_{ar}, J=8.3Hz), 8.19 (*d*, 4H, H_{ar}, J=8.3Hz), 8.06(*s*, 2H, NH), 3.92 (*s*, 6H, OCH_3), 3.08 (*m*, 4H), 1.18 (*t*, 4H). **FTIR**: 3300(NH), 3020(C_{sp2}-H), 2950(C_{sp3}-H), 1721(C=O ester), 1630(C=O amide), 1538(C=C).

*N,N',N''-tris-(4-methoxycarbonylbenzoyl)-1, 1, 1-tris-(amino methyl) ethane **(3d)**.* Yield: 51%. M.P.: 223-225ºC. **Anal. Elem.** $C_{33}H_{33}N_3O_9$: Calcd. C, 63.7; H, 5.5; N, 7.0. Found. C, 63.4; H, 5.4; N, 6.8. **^{1}H NMR**: 8.82 (*t*, 3H, NH), 8.11-8.00 (*d,d*, 12H, H_{arom}), 3.89 (*s*, 9H, OCH_3), 3.29 (*d*, 6H, CH_2), 0.91 (*s*, 3H, CH_3). **FTIR**: 3321(NH), 1724(C=O ester), 1648(C=O amide), 1538(C=C).

*N,N',N''-tris-(4-methoxycarbonylbenzoyl)-tris-(2-amino ethyl) amine **(3e)**.* Yield: 89 %. M.P.: 239-241ºC. **Anal. Elem.** $C_{33}H_{36}N_4O_9$: Calcd. C, 62.6; H, 5.7; N, 8.9. Found. C, 62.5; H, 5.5; N, 8.6. **^{1}H NMR**: 9.07 (*s*, 3H, NH), 7.95 (*d*, 6H, H_{ar}, J= 8.0Hz), 7.91 (*d*, 6H, H_{ar}, J=8.0Hz), 3.88 (*s*, 9H, OCH_3), 3.73 (*m*, 6H), 3.54 (*m*, 6H). **FTIR**: 3248 (NH), 2956 (C_{sp3}-H), 1723(C=O ester), 1670 (C=O amide), 1641 (C=C).

*Hydrolysis Procedure. Bis- and Tris-amides (**4a-e**).*

To a solution of **3a-e** (1.3 mmol) in 20 ml of methanol/water 2:1 mixture, KOH (0.29 g, 5.1 mmol) was added. The resulting mixture was refluxed with stirring during 3 h and then poured into 250 ml of an ice-10% HCl mixture, stirred and filtered. The white solid was filtered and washed with water and diethyl ether.

*N,N`-bis-(4-carboxybenzoyl)-1,2-ethanediamine. (**4a**).* Yield: 98%. M.P.: >330ºC. **Anal. Elem.** $C_{18}H_{16}N_2O_6$: Calcd. C, 60.7; H, 4.5; N; 7.9. Found. C, 60.2; H, 4.5; N; 7.9. **^{1}H NMR**: 13.19 (*s*, 1H, OH), 8.78 (*t*, 2H, NH), 8.01 (*d*, 4H, H_{ar}, J=6.8Hz), 7.94 (*d*, 4H, H_{ar}, J=6.8Hz), 3.46 (*d*, 4H). **FTIR**: 3303(NH), 3300-2500(OH acid), 3066(C_{sp2}-H), 2931(C_{sp3}-H), 2668 and 2554(Fermi), 1694(C=O acid), 1637(C=O amide), 1540(C=C).

*N,N`-bis-(4-carboxybenzoyl)-1,3-propanediamine. (**4b**).* Yield: 98%. M.P.: >330ºC. **Anal. Elem.** $C_{19}H_{18}N_2O_6$: Calcd. C, 61.6; H, 4.9; N; 7.6. Found. C, 59.9; H, 4.7; N; 7.5. **^{1}H NMR**: 8.65 (*t*, 2H, NH), 8.01 (*d*, 4H, H_{ar}, J=4.4Hz), 7.99 (*d*, 4H, H_{ar}, J= 4.4 Hz), 3.34 (*m*, 4H), 1.81 (*q*, 2H), 1.58 (*m*, 2H). **FTIR**: 3307(NH), 3300-2500(OH acid), 2950(C_{sp2}-H), 2864(C_{sp3}-H), 2672 and 2557 (Fermi), 1696(C=O acid), 1635(C=O amide), 1534 (C=C).

*N,N`-bis-(4-carboxybenzoyl)-1,4-butanediamine. (**4c**).* Yield: 99%. M.P.: >330ºC. **Anal. Elem.** $C_{20}H_{20}N_2O_6$: Calcd. C, 62.5; H, 5.2; N, 7.3. Found. C, 61.6; H, 5.1; N, 7.3. **^{1}H NMR**: 8.62 (*t*, 2H, NH), 8.00 (*d*, 4H, H_{ar}, J=8.4Hz), 7.93 (*d*, 4H, H_{ar}, J=8.4 Hz), 3.32 (*m*, 4H), 1.59 (*s*, 4H). **FTIR**: 3329(NH), 3300-2500(OH acid), 2946(C_{sp2}-H), 2871(C_{sp3}-H), 2661 and 2541 (Fermi), 1681(C=O acid), 1638 (C=O amide), 1531 (C=C).

*N,N',N''-tris-(4-carboxybenzoyl)-1, 1, 1-tris-(aminomethyl) ethane (**4d**).* Yield: 76%. M.P.: 313-315ºC. **Anal. Elem.** $C_{29}H_{27}N_3O_9$: Calcd. C, 62.0; H, 4.8; N, 7.5. Found. C, 60.9; H, 4.6; N, 7.5. **^{1}H NMR**: 8.80 (*t*, 3H, NH), 8.17 (*d*, 6H, H_{ar}), 8.10 (*d*, 4H, H_{ar}), 3.40 (*d*, 6H, CH_2), 2.60 (*broad signal*, 3H, OH), 1.01 (*s*, 3H, CH_3). **FTIR**: 3286(NH), 3300-2500(OH acid), 3173(C_{sp2}-H), 1712(C=O acid), 1640(C=O amide), 1540(C=C).

*N,N',N''-tris-(4-carboxybenzoyl)-tris-(2-amino ethyl) amine (**3e**).* Yield: 93%. M.P.: >330ºC. **Anal. Elem.** $C_{30}H_{30}N_4O_9$: Calcd. C, 61.0; H, 5.1; N, 9.5. Found. C, 60.7; H, 5.0; N, 9.4. **^{1}H NMR**: 13.14 (*s*, 2H, OH), 8.56 (*s*, 3H, NH), 7.94 (*d*, 6H, H_{ar}, J=8.0Hz), 7.87 (*d*, 6H, H_{ar}, J=8.4Hz), 3.32 (*s*, 6H), 2.77 (*s*, 6H). **FTIR**: 3356(NH), 3300-2500(OH acid), 3057(C_{sp2}-H), 2623(Fermi), 1715(C=O acid), 1646(C=O amide), 1541 (C=C).

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