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Chiral Bis(tyrosinol) and Bis(*p*-hydroxyphenylglycinol) Oxalamide Gelators. Influence of Aromatic Groups and Hydrogen Bonding on Gelation Properties*

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Enantiomerically pure *R,R*-bis(4-hydroxyphenylglycinol) oxalamides **3** and *S,S*-bis(tyrosinol) oxalamides **4** were prepared and tested for their gelling properties toward organic solvents, water and aqueous mixtures with polar organic solvents. It was found that oxalamide compounds with aryl substituted phenolic hydroxy groups are efficient organogelators of highly polar solvent systems while the derivatives with free phenolic hydroxy groups tend to crystallize. The revealed different behaviour is explained on the basis of specific hydrogen bonding motifs found in the crystal structures.

INTRODUCTION

There has been considerable recent interest in the development of new organogelators based on low molecular weight compounds. Many potential applications of gels as new »soft« materials are foreseen, for example, designing slow drug delivery systems,[1] development of sensing devices[2] or hardeners of liquid waste materials.[3] In recent years, a number of low molecular weight organic compounds have been reported to be effective gelators of various organic solvents, water and their mixtures. Supramolecular nature of gelation has been widely recognized. Gels are formed by predominantly unidirectional self-assembly of organic molecules and the driving forces involved are ion-ion and dipole-dipole electrostatic interactions, hydrogen bonding, van der Waals interactions, solvophobic and π-π stacking interactions. This results in the formation of fibers, tapes or strands, which entangle into a network capable to immobilize large volumes of liquids *via* surface tension and related forces.[4] In most cases, gels contain less than 5 % (*w*) of gelator and more than 95 % (*w*) of solvent. They are thermally reversible systems, and can repeatedly transform their physical state if not changed chemically; by heating they are transformed to a sol and by cooling again to gel.

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* Dedicated to Professor Nenad Trinajstić on the occasion of his 65th birthday.

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Despite enhanced research activity in this field during the past 10 years, it is still very difficult to predict gelation properties on the basis of chemical structure. The organogelators reported up to now display a wide structural diversity, including amino acid or peptide derivatives,[5] ureas,[6] sugars,[7] steroids,[8] nucleic acids,[9] aromatic compounds,[10] gemini surfactants,[11] two–component systems,[12] fullerene,[13] calixarene,[14] and porphyrine[15] derivatives, *etc*.

We have developed a versatile group of bis(amino acid) oxalamide gelators possessing a strongly hydrogen bonding and self-complementary oxalamide unit.[16–19] It has been shown that some of the prepared compounds show rather rare ambidextrous gelation properties, being capable of forming gels with lipophilic solvents but also with highly polar solvents and water.

As part of a systematic study of the relationship between gelation properties and gelator structure, we have prepared a series of bis(amino alcohol) oxalamide derivatives incorporating valinol, leucinol, phenylglycinol and phenylalaninol (Chart 1). It was found that such derivatives also possess excellent gelling properties, however considerably different from those of the structurally closely related bis(amino acid) oxalamides.[19]

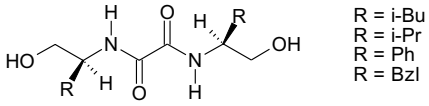
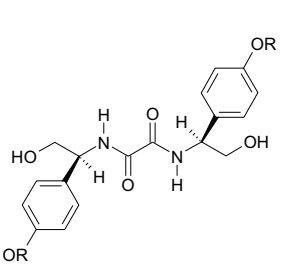


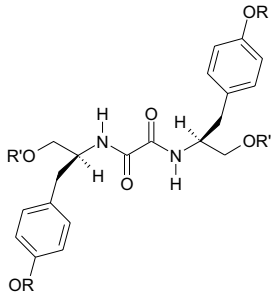
Chart 1.

It was found that the gelling properties of the two types of oxalamide gelators investigated are very susceptible to changes of their molecular structure and stereochemistry. Even small structural variations can cancel the gelling ability. The three types of associations are identified as decisive for gelation: the intermolecular hydrogen bonding between oxalamide units in combination with hydrogen bonding of the lateral functional groups (COOH, $CONH_2$ or CH_2OH), and lipophilic interactions between the substituents on asymmetric centres. In most cases, such interactions lead to formation of bilayers in water or inversed bilayers in organic solvents.[17,19] Dominating driving forces for the self-assembly are hydrophobic interactions in water and intermolecular hydrogen bonding in organic solvents.

The bis(aminoalcohol) oxalamides constructed from tyrosinol and *p*-hydroxyphenylglycinol possess phenolic and methylene hydroxy groups that can participate in intermolecular hydrogen bonding and also offer the possibility of further synthetic modifications by attachment of various aromatic or aliphatic substituents. Both possibilities may end in new gelators with improved properties. Here, we report the preparation of tyrosinol and *p*-hydroxyphenylglycinol derivatives **3** and **4** possessing: i) substituted phenolic OH and free alkyl OH group, ii) both OH groups free, and iii) both OH groups substituted. We also report the second structural modification, aimed to enhance the intermolecular aromatic stacking interactions; the derivatives with benzyl, naphthyl and biphenyl groups attached on phenolic oxygens are prepared (Chart 2). The capacity of these new gelators to form gels with organic solvents, water and their combinations are evaluated, and the microscopic and spectroscopic characteristics of the gels are reported.



(*R*,*R*)-**3a** R = Bzl
(*R*,*R*)-**3b** R = H



(*S*,*S*)-**4a** R = Bzl, R' = H
(*S*,*S*)-**4b** R = Me, R' = H
(*S*,*S*)-**4c** R = H, R' = H
(*S*,*S*)-**4d** R = Bzl, R' = Ac
(*S*,*S*)-**4e** R = Bzl, R' = Bz
(*S*,*S*)-**4f** R = 1-naphthylmethyl, R' = H
(*S*,*S*)-**4g** R = 2-naphthylmethyl, R' = H
(*S*,*S*)-**4h** R = 4-biphenylmethyl, R' = H

Chart 2.

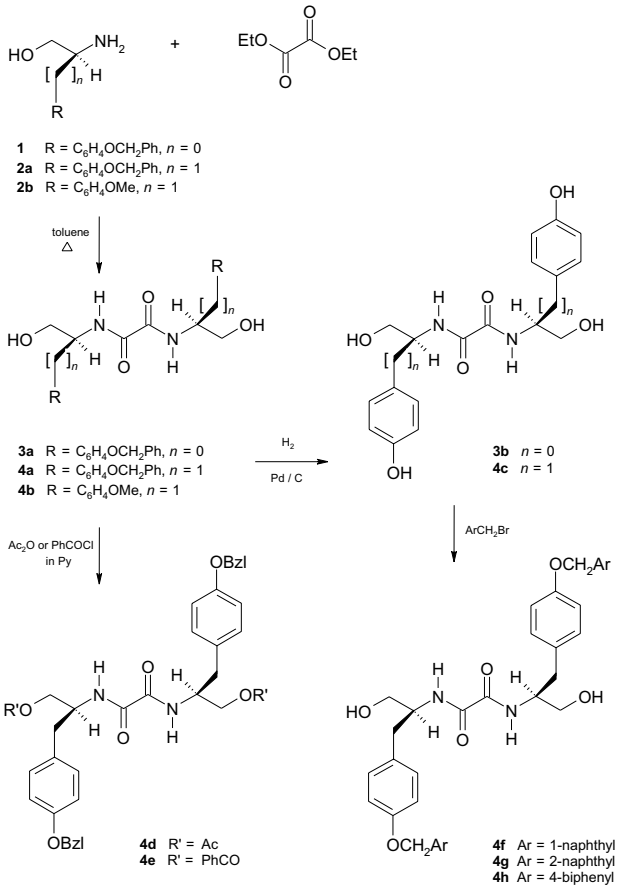
RESULTS AND DISCUSSION

Synthesis

The required optically active oxalyl dihydroxy diamides (Chart 2) were prepared according to Scheme 1, starting from previously synthesized amino alcohols, 2-amino-2-(4-benzyloxyphenyl)ethanol (**1**), 2-amino-3-(4-benzyloxyphenyl)propan-1-ol (**2a**) and 2-amino-3-(4-methoxyphenyl)propan-1-ol (**2b**) stemming from *R*-4-hydroxyphenylglycine and *S*-tyrosine.[20] Amino alcohols **1** and **2a**,**b** were reacted with diethyl oxalate to give oxalamides **3a** and **4a**,**b**. Hydrogenolysis of benzyl group in **3a** and **4a** gave hydroxy derivatives **3b** and **4c**. Aliphatic hydroxyl function in **4a** was acylated to give acetyl (**4d**) and benzoyl (**4e**) derivatives.

N,*N'*-Bis[1-hydroxymethyl-2-(4-hydroxyphenyl)ethyl] oxalamide (**4c**) served as precursor for aromatic derivatives **4f** and **4g**. Naphthyl substituents were introduced by the alkylation using the corresponding bromomethylnaphthalene, giving 1-naphthyl derivative **4f** and 2-naphthyl derivative **4g**.

Attempts to introduce biphenyl substituents using commercially available 4-chloromethylbiphenyl and K_2CO_3 as the base, gave only unreacted starting material, while in the presence of KI only phenyl-benzyl iodide was iso-



Scheme 1.

lated. Successful introduction of biphenyl substituent was achieved with 4-bromomethylbiphenyl (84 % yield), which was prepared previously by bromination of 4-methylbiphenyl with NBS in CCl_4 in the presence of dibenzoyl peroxide.

Gelation Experiments

Gelation behaviour of the prepared oxalamide compounds was tested against the following solvents or solvent mixtures: water, DMSO–water and DMF–water, EtOH, dioxane, THF, EtOAc, acetone, CH_2Cl_2, CH_3CN, toluene, and benzene. Due to poor solubility of the prepared derivatives in most of the listed solvents, it was necessary to use a minimal volume of DMSO as a cosolvent. In a typical experiment, measured volumes (100 μl) of the tested solvent were added with a syringe to the weighed amount (10 mg) of the tested gelator in a septum-capped 11 × 133 mm test tube. After each solvent addition, the mixture was heated up to the boiling point, and the resulting solution was then allowed to cool by immersing the test tube into a water bath (20 ± 2 °C). If the formation of a gel was observed, the procedure was repeated until the test tube could be inverted without noticeable flow.

In the case of low or too high solubility, gelation of solvent mixtures was performed. Such gelation experiments resemble a mixed solvent recrystallization. A gelator (10 mg) was dissolved in the measured minimal volume of a solvent where it was highly soluble, measured volumes of another less polar solvent were successively added, and the mixture was heated and cooled as above. The procedure was repeated until the mixture failed to form a gel.

We have observed that the gelling efficiency, expressed as the maximum volume of a solvent that could be gelled by 10 mg of gelator, significantly depends on the diameter (ϕ) of the test tube used. In a narrower tube, a considerably larger volume of solvent could be gelled than in a wider tube. We have performed gelation experiments in tubes of different diameters (ϕ = 4 –18 mm) with bis(leucinol) oxalamide (Chart 1) and bis(*p*-hydroxyphenylglycinol) oxalamide (**3a** in Chart 2) in EtOH and toluene, respectively. It was found that 10 mg of leucinol derivative entrapped 5.4 ml of toluene in a 16.3 mm test tube and close to an 8 times larger volume (42.6 ml) in a 4 mm test tube. Similarly, 10 mg of **3a** gelled 9 ml of ethanol in the 20 mm test tube and 34.9 ml in the 4.1 mm test tube. The results of these experiments, showing a practically linear dependence of the minimal gelation concentration c (mol dm^{-3}) on test tube diameter, are shown in Figures 1a,b.

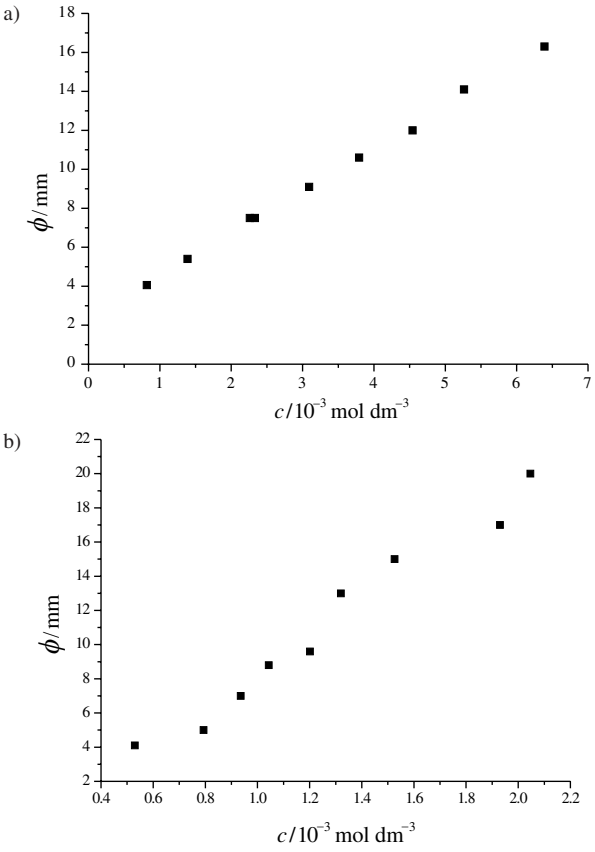


Figure 1. Relationship between test tube diameter (ϕ / mm) and gelation efficiency expressed as minimal gelation concentration c (mol dm^{-3}) determined for a) bis(leucinol) oxalamide-toluene gels, and b) bis(4-benzyloxyphenylglycinol)oxalamide (**3a**) – EtOH gels.

TABLE I. Gelation efficiency of various solvents and solvent mixtures by 10 mg of tested gelator expressed as the maximal volume (V_{max}) of gelled solvent or solvent mixture

solvent	V_{max} / ml									
	3a	**3b**	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**
H_2O	ns	A*	ns	ns	7.5*, A*	ns	ns	ns	ns	ns
DMSO + H_2O	7.90 + 5.40	A*	10.00 + 9.05	cr	0.20 + 2.00	1.35 + 3.15	A*	cr	7.10 + 9.00	12.5 + 6.10 or 0.75 (b)
DMF + H_2O	9.75 + 11.00	cr	2.55 + 4.65	cr	0.20 + 2.25, A*	1.72 + 0.53	A*	cr	6.40 + 10.20	9.00 + 3.35
EtOH +	10.50	cr	1.40 + 0.10 (b)	cr	0.30	5.25	ns	cr	cr	1.40 + 0.10(b)
CH_3CN +	+b, cr*	cr	ns	cr	1.85, A*	1.65	ng	ns	+b, cr	1.44 + 0.30(b)
acetone +	A*	ns	+b, s	cr	s	s	+a, cr	ns	0.250 + 0.01(b)	+b, cr
EtOAc +	A*	ns	+b, s	cr	ns	0.80	+a, cr	cr	+b, cr	+b, cr
dioxane +	0.55	cr	1.15 + 1.10(a)	cr	+a,cr	cr	0.30	+b, A*	0.45	0.35
THF +	0.60	ns	2.00 + 2.55(a)	cr	0.55 + 0.25(a)	cr	0.40	cr	+a, cr	cr
CH_2Cl_2 +	3.35	ns	ns	ns	0.35 + 0.01(b)	cr	0.25	3.50	+b, cr	0.30 + 0.05 (b)
toluene +	3.75	ns	8.90	4.50	ns	1.50	1.50	8.90	+b, cr	4.40 + 0.05 (b)
other	–		benzene 3.60	benzene A*			THF–EtOH 0.40 + 0.10			

Abbreviations: ng – no gelation; ns – not soluble; s – solution; cr – crystallization; a – hexane; b – DMSO; A*– unstable gel, tends to crystallize; *gelation needs rapid cooling at +15 °C.

Due to the observed dependence of gelling efficiency on the test tube diameter, and to allow comparison with other gelators and solvents, the V_{max} values shown in Table I were determined using 11x133 mm test tubes for V_{max} < 8.5 ml, 15x160 mm test tubes for V_{max} 8.5–18 ml and 19x200 mm test tubes for V_{max} >18 ml.

Most of the tested oxalamides formed thermally reversible gels with organic solvents or their mixtures and only **4c** also with water but only after rapid cooling to 15 °C. The oxalamides **3b** and **4c** possessing free phenolic and alkyl OH groups failed to gel (**3b**) or exhibited only weak gelation (**4c**) of the solvents and solvent mixtures tested (Table I). It was observed for both derivatives that the initially formed weak gels rapidly transformed to crystals. These observations suggest that the presence of free phenolic and alkyl OH groups in **3b** and **4c**, capable of providing additional intermolecular hydrogen bonds, make these derivatives prone to crystallization. In contrast, the benzylated *p*-hydroxyphenylglyicinol (**3a**) and tyrosinol (**4a**) oxalamides, exhibited excellent gelation of highly polar DMSO–water and DMF–water systems and also weak to modest gelation of more lipophilic solvents such as dioxane, THF and toluene (Table I). Interestingly, **3a** efficiently gelled also ethanol. In contrast, the **4b** derivative with methyl instead of benzyl groups on phenolic oxygens of **4a** failed to gel any of the tested solvents except toluene. Comparison of the gelation properties of compounds **3a**, **4a**; **3b**, **4c** with that of **4b** suggests that the presence of benzyl substituents on phenolic oxygens of the former enhance gelation compared to **3b**, **4c** with free phenolic OH's, but the presence of methyl (**4b**) instead of benzyl groups strongly reduces the gelation ability. For derivatives **4d** and **4e** with both types of OH groups blocked, a strong reduction of gelling property was also observed if compared to **4a**. Since the benzyl derivatives **3a** and **4a** showed improved gelation properties compared to unsubstituted **3b** and **4c**, it was assumed that the intermolecular aromatic stacking interactions might be responsible for the enhanced gelation. Hence, the derivatives **4f–h** bearing larger aromatic substituents were prepared.

The bis(1-naphtyl) derivative **4f** is capable of modest gelation of toluene and fails to gel any of the other solvents tested. However, bis(2-naphtyl) derivative **4g** and bis(biphenyl) derivative **4h** exhibited very efficient gelation of DMSO– and DMF–water mixtures, and weak to moderate gelation of toluene. Compared to unsubstituted **4c**, both **4g** and **4h** are superior gelators, capable to immobilize 8 times larger volumes of DMSO– and DMF–water mixtures. The striking difference of gelation ability observed for 1-naphtyl and 2-naphtyl derivatives **4f** and **4g**,

respectively, is indicative of structural factors being very important for gelation.

In conclusion, among all the prepared oxalamide derivatives, the best gelling properties exhibited *p*-hydroxyphenylglycinol and tyrosinol derivatives possessing aromatic substituents on phenolic oxygens: benzyl derivatives **3a** and **4a**, β-naphtyl derivative **4g** and biphenyl derivative **4h**. These derivatives are very efficient gelators of the highly polar DMSO–water and DMF–water mixtures; their minimal gelation concentrations are: 4.8 × 10^{-4} g cm^{-3}, **3a** (DMF–water); 5.2 x 10^{-4} g cm^{-3}, **4a** (DMSO–water); 6.0 x 10^{-4} g cm^{-3}, **4g** (DMF–water), and 5.4 x 10^{-4} g cm^{-3}, **4h** (DMSO–water).

Gel Morphology; TEM and SEM Observations

Typical gel morphology was observed by electron microscopy. Figure 2 displays TEM images of **4c** and **3a** gels, and SEM micrographs of **4c** hydrogel and crystalline fibers of **3b** formed in the DMF–water system. TEM shows the presence of highly intertwined fibers with diameters in the range of 10–55 nm constituting a dense network of **4c** hydrogel (Figure 2a); SEM imaging of the same gel shows that the network is three-dimensional (Figure 2b). The TEM micrograph of the **3a**–ethanol gel shows that it consists of a much less dense network, formed by fiber bundles of diameters in the range of 100–400 nm.

It is important to note that a gel-like structure consisting of large entangled crystalline fibers can be formed under controlled experimental conditions. If the DMF solution of **3b** in an open vessel is immersed into a larger vessel containing water, very slow water evaporation and mixing with DMF results in the formation of a thin gel layer at the surface. After several days, a non-transparent gel-like system is formed within the whole volume. The cotton-like network is observable under a light microscope; the SEM image of the network (Figure 2d) shows that it consists of crystalline fibers of larger diameters (100–400 nm). This observation indicates that the gel fibers formed at the surface layer may induce crystallization into crystalline fibers of nanometer size. Further investigations aimed to prove this possibility are in progress and the findings could be of interest for the production of organic nano-fibers.

Spectroscopic Investigations

In the FTIR spectrum of the 5.87 x 10^{-2} mol dm^{-3} THF solution of **3a,** the ν_{NH} and amide I bands appear at 3397 cm^{-1} and 1681 cm^{-1}, respectively. The positions of these bands are characteristic of non-hydrogen bonded oxalamide units. In the amide II region, two shoulders could be detected, at 1511 cm^{-1} and 1500 cm^{-1}, partly overlapped by the broad THF band at 1459 cm^{-1}. However, in the THF gel spectrum at a 2.62 x 10^{-2} mol dm^{-3} concentration of **3a**, two ν_{NH} bands are present: the one at 3397 cm^{-1} of free, non-hydrogen bonded NH's and the one at 3292 cm^{-1}, being characteristic of hydrogen bonded NH's. Also the two amide I bands (free at 1681 cm^{-1} and hydrogen bonded at 1654 cm^{-1}) and two amide II bands (at 1511 cm^{-1} and 1500 cm^{-1}) can be observed. Similar positions of the free and associated ν_{NH} and amide I bands can be found also in the spectra of **4d**–toulene and **4c**–dioxane gels. The spectra of gels show clear temperature dependence. Figure 3 illustrates the changes ob-

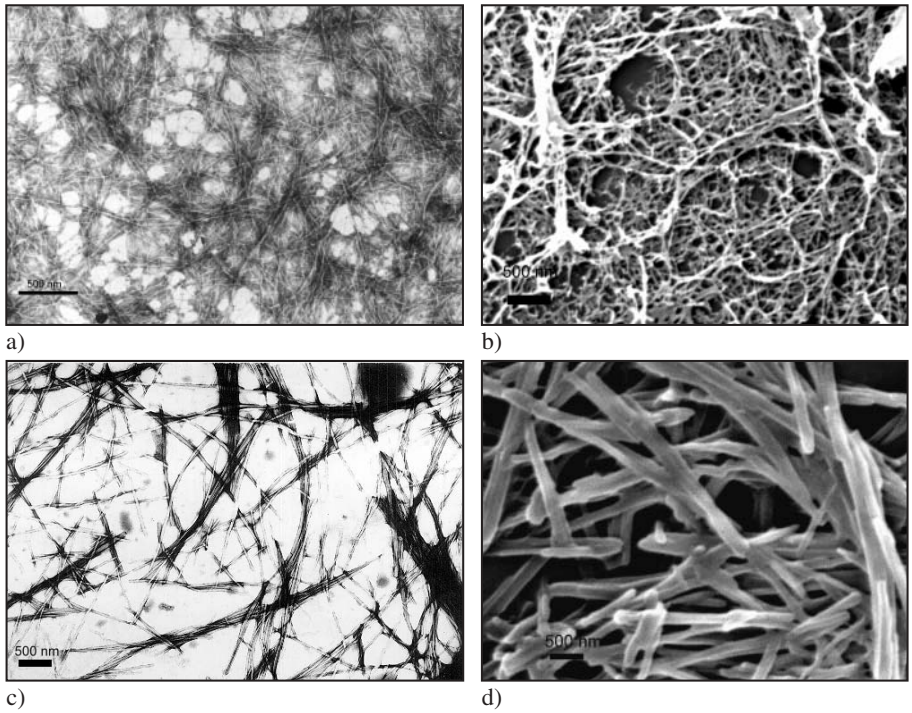


Figure 2. a) TEM micrograph of **4c** hydrogel (6 × 10^{-3} g cm^{-3}) negatively stained with PWK; b) SEM micrograph of **4c** hydrogel (9 × 10^{-3} g cm^{-3}); c) TEM micrograph of **3a** EtOH gel (4.5 × 10^{-3} g cm^{-3}); d) SEM micrograph of crystalline fibers of **3b** from DMF–water

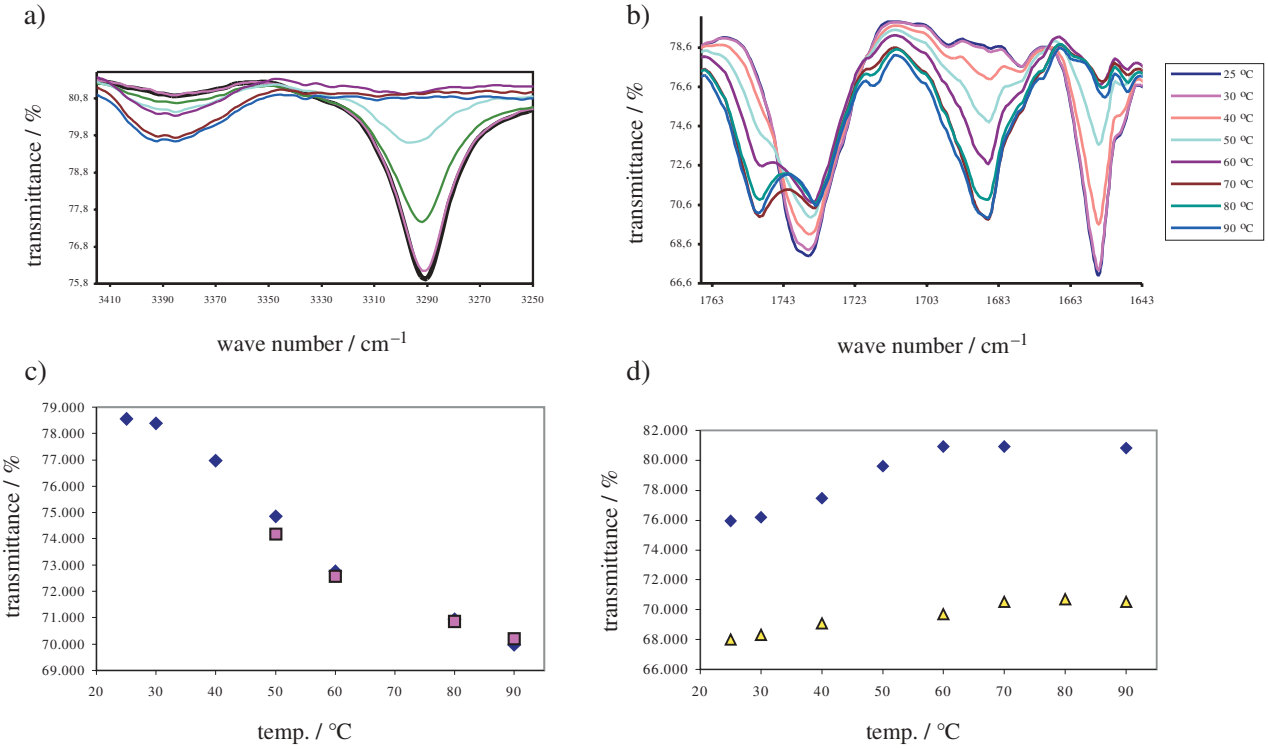


Figure 3. Temperature dependent FTIR spectra of **4d** in toluene; a) NH regions, b) carbonyl regions, c) intensity changes of ◆ amide I (free)., □ NH (free) and d) intensity changes of ◆ NH (assoc.)., Δ CO (assoc.).

served in the spectra of **4d**–toulene gel in the temperature range of 25–90 °C; with temperature increase, the intensities of hydrogen bonded NH and amide I bands decreased while those of free, non-hydrogen bonded functionalities appearing at higher wave numbers increased. These observations clearly show that oxalamide functionalities are involved in intermolecular hydrogen bonding that stabilizes gel fibers.

The temperature dependent ^{1}H NMR spectra of **3a**–THF, **4a–**dioxane/cyclohexane and **4h**–DMSO/water gels show significant upfield shifts of NH protons with increasing temperature. Such upfield shifts are interpreted by dissociation of intermolecularly hydrogen bonded aggregates involving oxalamide units (Figure 4).[17,18] The NH temperature coefficients $\Delta\delta/\Delta T$ of 5.3×10^{-3}, 3.4×10^{-3} and 2.8×10^{-3} ppm K^{-1} have been determined for **4h**, **3a** and **4a** gels; the values show the highest temperature induced shifts for NH protons of **4h** gel formed in the DMSO/water system, which is capable to strongly compete with intermolecular oxalamide hydrogen bonding. Smaller coefficients were obtained for **3a** and **4a** gels containing more lipophilic and less competitive solvents. Surprisingly, a very small coefficient was determined for **3a** OH protons ($\Delta\delta/\Delta T = 0.7 \times 10^{-3}$ ppm K^{-1}); this can be interpreted either by the absence of intermolecular OH·····OH hydrogen bonding in the aggregates or by only a slight chemical shift difference of hydroxyl protons involved in OH·····OH and OH·····O–THF hydrogen bonding.

In the temperature dependent spectra of **3a**–THF and **4a**–dioxane-d_8/cyclohexane-d_{12} gels, the signals of aromatic protons are only slightly shifted upfield. These observations are inconclusive since in the case of intermolecular aromatic stacking interactions in the aggregates, aromatic protons should be significantly shifted downfield by disaggregation.

In conclusion, both the temperature-induced changes in FTIR and ^{1}H NMR spectra of selected gels clearly point

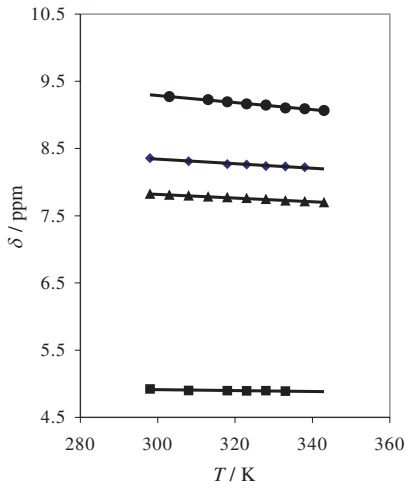


Figure 4. Temperature induced chemical shift changes in the ^{1}H NMR spectra: (●) NH's of **4h**-DMSO-d_6/D_2O (2:1, vol.) gel; (◆) NH of **3a**-THF gel; (▲) NH's of **4a**-dioxane-d_8/cyclohexane-d_{12} (1.5:1, vol.) gel and (■) OH's of 3a-THF gel.

TABLE II. Hydrogen bond geometry of the three-dimensional γ-network

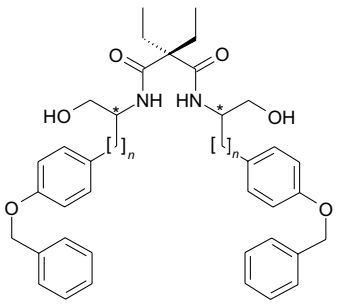
D – H···A	D – H / Å	H···A / Å	D···A / Å	∠ D – H···A / °	Symmetry operation on A
N1–H1···O11	0.86	2.33	2.715(3)	107	*x*, *y*, *z*
N1–H1···O21	0.86	2.07	2.853(3)	152	1+*x*, *y*, *z*
O2–H2···O31	0.82	2.10	2.900(3)	165	–*x*, 1/2+*y*, –z
O3–H3···O1	0.82	1.89	2.708(3)	179	–*x*, –1/2+*y*, 1–z
N11–11···O1	0.86	2.26	2.648(3)	108	*x*, *y*, *z*
O21–21···O2	0.82	1.94	2.737(4)	164	–1+*x*, –1+*y*, *z*
O31–31···O11	0.82	1.87	2.674(3)	167	–*x*, 1/2+*y*, –*z*

to intermolecular hydrogen bonding between oxalamide units in the aggregates constituting gel fibers in highly polar DMSO–water as well as in the lipophilic solvent mixtures. These observation are in accord with those previously found for the structurally closely related bis(amino acid) and bis(aminoalcohol) oxalamide gelators.[17,18]

*Molecular and Crystal Structure of **3b***

Among the crystal structures of *N*,*N*′-bis(amino acid) oxalamides[17,18] and their derivatives there is a single example of a three-dimensional hydrogen bonded **3b** γ-network: (*R*,*R*)-**3b** oxalamide reveals an entirely different system of hydrogen bonds. According to experience in crystal engineering of using oxalamide, carboxyl, hydroxy or amide groups as synthons, there are preferences for hydrogen bonding.[21] One-dimensional α-network though is created *via* oxalamide groups whereas terminal donor and acceptor groups participate in hydrogen bonding completing a two-dimensional β-network.[17,21] However, a three-dimensional γ-network can be obtained by inserting additional donor/acceptor groups in-between the oxalamide bridge and the termini of a molecule. Thus, the additional synthon participates in the formation of the three-dimensional network. Introducing PhOH groups on both sides of the oxalamide bridge, two additional OH groups contribute to hydrogen bonding. Intensive hydrogen bonding stabilized the crystal lattice and very good quality crystals were obtained. In contrast to other oxalamide derivatives studied, which involve a one-dimensional hydrogen bonded 'ladder' pattern acting between oxalamide groups, the *p*-hydroxyphenyl analogue **3a** does not reveal such a pattern. Instead, the N1H of oxalamide, both terminal hydroxy groups and one of tyrosyl moiety exchange donor and acceptor functions: N1H → O21H → O2H → O31H → O11, and O3H → O1. Thus, hydrogen bonds act between oxalamide and terminal hydroxy groups, between terminal hydroxy groups, between hydroxy groups of PhOH moieties and oxalamide carbonyl groups, and finally between hydroxy groups of PhOH and the terminal ones. (Table II, Figure 5). It is interesting that one of oxalamide amide groups (N11H) does not participate in intermolecular hydrogen bonds, the closest neighbour is O3 at 3.470 Å but the angle is not favourable for hydrogen bonding (less than 90°). However, the typical intramolecular N–H···O hydrogen bonds, including both N1H and N11H, form *pseudo*-C_5 rings like in all crystal structures of oxalamide derivatives solved.

The PhOH groups are *trans*-oriented with respect to the oxalamide bridge. Hence, the intramolecular π···π interactions are not feasible. However, there are CH···π interactions between one of the methylene groups and the aromatic ring operated by 1–*x*, 1/2+*y*, 1–*z* with the hydrogen to centroid (of the aromatic ring) separation distance of 2.966 Å. There are also CH···π interactions with the corner to centroid separation distances of 2.978 and 3.001 Å of two neighbouring aromatic rings of molecules related by a screw two-fold axis and a translation.



5a *n* = 0
5b *n* = 1

Chart 3.

CONCLUSIONS

We present evidence that *p*-hydroxyphenylglycinol and tyrosinol derivatives possessing aromatic substituents on phenolic oxygens, such as benzyl derivatives **3a** and **4a**, β-naphtyl derivative **4g** and biphenyl derivative **4h,** are efficient gelators of highly polar DMSO– or DMF–water mixtures and moderate gelators of lipophilic solvents CH_2Cl_2 and toluene. Compared to **3b** and **4c** possessing free phenolic OH groups, the former molecules are much more efficient gelators capable of immobilizing up to 8

times larger volumes of solvents. However, compound **4b** with methyl substituents on phenolic OH groups failed to gel any of the tested solvents and solvent mixtures except toluene. This observation suggests that aromatic substituents on phenolic oxygens play an important role in gelation; however, no spectroscopic evidence was found for intermolecular aromatic stacking interactions in the aggregates. Spectroscopic investigations showed that intermolecular hydrogen bonding between oxalamide units stabilizes gel aggregates in highly polar and in lipophilic solvent systems. It was observed that **3b** with free phenolic OH groups have a strong tendency to crystallization or initially form unstable gels that rapidly turn to crystals. The determined molecular and crystal structure of **3b** provides explanation of such behaviour. In contrast to all previously determined molecular structures of bis(aminoacid) and bis(aminoalcohol) oxalamide gelators,[17,19] which show *cis*-arrangement of substituents on asymmetric carbons, the *trans*-arrangement of *p*-hydroxyphenyl substituents was found for **3b**. Also in contrast to β-hydrogen bonded network found in the crystal structures of bis(aminoacid) and bis(aminoalcohol) oxalamide gelators, **3b** formed a three dimensional γ-network lacking the intermolecular oxalamide-oxalamide pairing. The

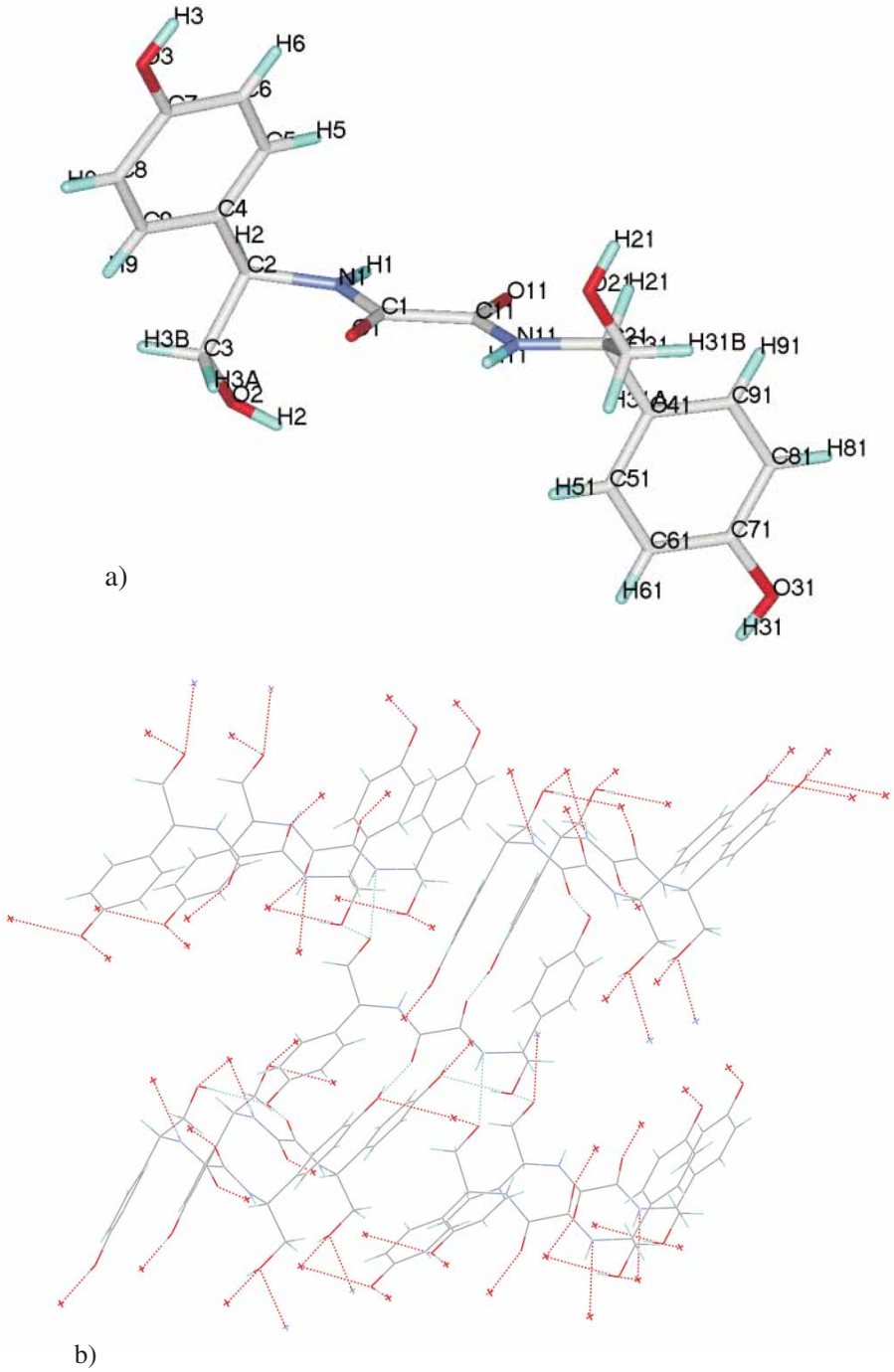


Figure 5. The molecular structure (a) and the three-dimensional γ-network (b) found in the crystal of **3b**.

latter, however, presents the basic motif in all the previously determined crystal structures, being responsible for unidirectional self-assembly into fibrous aggregates.[17,19] Apparently, the presence of additional hydrogen bonding functionalities (phenolic OH's) in **3b** led to a complete change of the intermolecular hydrogen bonding pattern. The molecular structure of **3b** with *trans*-oriented phenolic units was formed to ensure formation of the maximal number of intermolecular hydrogen bonds. As a consequence, the formation of the three-dimensional γ-network with altogether 10 intermolecular hydrogen bonds led to crystallization. It should be noted that the tyrosinol derivative **4c**, differing from **3b** only in having more flexible *p*-hydroxybenzyl instead *p*-hydroxyphenyl substituents on asymmetric carbons, still retained weak gelation ability. The latter represents a remarkable illustration how very subtle structural differences could have a decisive influence on gelation properties.

EXPERIMENTAL

Reagents were purchased from Aldrich or Fluka and were used without further purification. All solvents were purified and dried according to standard procedures. Thin-layer chromatography (t.l.c.) was performed on Merck Kieselgel HF_{254} plastic sheets and spots were made visible using a UV lamp (254 nm) or I_2 vapours. Preparative t.l.c. was performed on silica gel (type 60 F_{254}, Merck), the plates were activated at 110 °C for 1 h. Melting points were determined on an Electrothermal Melting Point Apparatus 9100 in capillary tubes and were not corrected. Optical rotations were measured on an Optical Activity AA-10 Automatic Polarimeter in a 1 dm cell at 589 nm, concentrations were given in g/100 ml. IR spectra were taken in KBr pellets on a Perkin Elmer 297 spectrometer, ν in cm^{-1}. FTIR experiments on gels were performed in sealed heatable cells for liquids (Specac, type 2051, path length 0.05 mm, KBr windows) and recorded on a ABB Bomen MB 102 FTIR-spectrometer, equipped with CsI optics, DTGS detector and Specac 3000 Series high stability temperature controller with 21-20730 heating jacket. NMR spectra were recorded on a Varian XL-300 Gemini spectrometer at 300/75 MHz, in DMSO-d_6. Chemical shifts (δ) were given in ppm, J in Hz. Mass spectra were recorded on Extrell FTMS 2001-DD Fourier Transform Mass Spectrometer electron impact, ionizing voltage 70 eV. The preparation of aminoalcohols **1, 2a** or **2b** was reported previously.[20] Some compounds (**4f**, **4g** and **4h**) were too insoluble to be purified satisfactorily for elemental analysis, so they were analyzed as acetyl derivatives.

*General Procedure for the Preparation of Oxalyl-dihydroxy-diamides **3a, 4a** and **4b***

The appropriate amino alcohol **1, 2a** or **2b** (4 mmol) was suspended in toluene (10–20 ml), and diethyl oxalate (2 mmol) was added under vigorous stirring. The reaction mixture was refluxed under vigorous stirring for 1 hour. Very soon in the heating to reflux period, the solution was formed, which quickly transformed to a dense gelatinous mass. After cooling to room temperature, the mixture was diluted with methanol (15–25 ml) until the gelatinous mass was destroyed, and the crystalline product was obtained, which was separated by filtration.

(R,R) N,N'-*Bis{1-[4-(benzyloxy)phenyl]-2-hydroxyethyl}ethanediamide (**3a**)*

From **1**: 75 %; R_F *ca.* 0.45 (CH_2Cl_2:MeOH 19:1); m.p. 230–232 °C (from DMSO–MeOH); $[\alpha]_D^{20}$ = –111 (c = 1.0 g/100 ml, DMSO); IR (KBr) $\nu_{max.}/cm^{-1}$: 3355, 3270, 1648, 1610, 1584, 1508; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.95 (d, 2H, J = 8.5 Hz, NH), 7.41–7.28 (m, 10H, (CH_2)PhH) 7.24 (d, 4H, J = 8.5 Hz, OPhH–2'), 6.91 (d, 4H, J = 8.5 Hz, OPhH–3'), 5.04 (s, 4H, OCH_2(Ph)), 4.90 (br s, 2H, OH), 4.85–4.78 (m, 2H, *CH), 3.69 and 3.59 (dd as t, 2H, J = 10.5 Hz, (HO)–CHa(Hb)); dd, 2H, J = 5.0; 10.5 Hz, (HO)–C(Ha)Hb); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.83 (CO), 157.21 (OPhC–4'), 137.26 (1C, O(CH_2)–Ph), 132.65 (OPhC–1'), 128.56(OPhC–2'), 128.35, 127.91, 127.73 (5CH, O(CH_2)–Ph), 114.57 (OPhC–3'), 69.27 (OCH_2(Ph)), 64.10 (CH_2OH), 55.28 (*CH).

Anal. Calcd. for $C_{32}H_{32}N_2O_6$ x H_2O (M_r = 558.61): C 68.80, H 6.13, N 5.01 %; found: C 68.60, H 6.07, N 5.12 %.

(R,R) N,N'-*Bis{1-[4-(benzyloxy)benzyl]-2-hydroxyethyl}ethanediamide (**4a**)*

From **2a**: 74 %; R_F *ca.* 0.35 (CH_2Cl_2:MeOH 19:1); m.p. 210–212 °C (from DMSO-MeOH); $[\alpha]_D^{20}$ = –45 (c = 1 g/100 ml, DMSO); IR (KBr) $\nu_{max.}/cm^{-1}$: 3365, 3270, 1650, 1610, 1582, 1508; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.34 (d, 2H, J = 9.0 Hz, NH), 7.40–7.11 (m, 10H, –(CH_2)–PhH), 7.06 (d, 4H, J = 8.5 Hz, OPhH–2'), 6.86 (d, 4H, J = 8.5 Hz, OPhH–3'), 4.99 (s, 4H, –OCH_2–(Ph)), 4.90 (br s, 2H, OH), 3.90 (m, 2H, *CH), 3.37 (m, 4H, CH_2(OH)), 2.77 and 2.64 (dd, 2H, J = 5.0; 14.0 Hz, *C(H)–CHa(Hb), dd, 2H, J = 8.5; 14.0 Hz, *C(H)–C(Ha)Hb); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.64 (CO) 156.85 (OPhC–4'), 137.29 (1C, O(CH_2)–Ph, 131.04 (OPhC–1'), 130.10 (OPhC–2'), 128.52, 127.90, 127.81 (5CH, O(CH_2)–Ph), 114.54 (OPhC–3'), 69.25 (OCH_2(Ph)), 62.29 (CH_2OH), 53.30 (*CH), 35.35 (–(*CH)CH_2–).

Anal. Calcd. for $C_{34}H_{36}N_2O_6$ (M_r = 568.65): C 71.81, H 6.38, N 4.93 %; found: C 71.68, H 6.14, N 5.11 %.

(S,S) N,N'-*Bis[2-hydroxy-1-(4-methoxybenzyl)ethyl]-ethanediamide (**4b**)*

From **2b**: 62 %; R_F *ca.* 0.37 (CH_2Cl_2:MeOH 19:1); m.p. 205–206 °C (from MeOH); $[\alpha]_D^{20}$ = –58 (c = 1.0 g/100 ml, DMSO); IR (KBr) $\nu_{max.}/cm^{-1}$: 3360, 3280, 1640, 1608, 1576, 1500; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.31 (d, 2H, J = 9.0 Hz, NH), 7.04 (d, 4H, J = 8.5 Hz, OPhH–2'), 6.77 (d, 4H, J = 8.5 Hz, OPhH–3'), 4.86 (br s, 2H, OH), 3.89–3.73 (m, 2H, *CH), 3.68 (s, 6H, OCH_3), 3.61–3.36 (m, 4H, (HO)CH_2), 2.76 and 2.63 (dd, 2H, J = 5.3; 14.0 Hz, (HO)–CHa(Hb) and dd, 2H, J = 8.5; 14.0 Hz, (HO)–C(Ha)Hb); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.64 (CO), 157.70 (OPhC–4'), 130.75 (OPhC–1'),

130.07 (OPhC–2'), 113.69 (OPhC–3'), 62.32 (CH_2OH), 55.03 (OCH_3), 53.30 (*CH), 35.33 ((*CH)CH_2).

Anal. Calcd. for $C_{22}H_{28}N_2O_6$ (M_r = 416.46): C 63.44, H 6.78, N 6.73 %; found: C 63.62, H 6.85, N 6.87 %.

*General Procedure for the Preparation of Oxalyl-dihydroxy-diamides **3b** and **4c***

To a solution of the benzyloxy compound **3a** or **4a** (1 mmol) in methanol (55 ml), 10 % palladium on activated carbon (40 mg) was added and stirred in an H_2 atmosphere at 10^4 hPa at 40 °C for 2 h. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was triturated with dichloromethane–methanol (10:1) and diethyl ether to give the crystalline product **3b** or **4b.**

(R,R) N,N'-*Bis[2-hydroxy-1-(4-hydroxyphenyl)ethyl]-ethanediamide (**3b**)*

From **3a**: 93 %; R_F *ca.* 0.69 (CH_2Cl_2:MeOH 7:3); m.p. 244–245 °C (from H_2O); $[\alpha]_D^{20}$ = –132 (*c* = 1.0 g/100 ml, MeOH); IR (KBr) $\nu_{max.}$/cm^{-1}: 3441, 3372, 3298, 3237, 1670, 1650, 1617, 1511; ^{1}H NMR (DMSO-d_6) δ/ppm: 9.27 (s, 2H, OH–(Ph)), 8.82 (d, 2H, *J* = 8.6 Hz, NH), 7.09 (d, 4H, *J* = 8.3 Hz, OPhH–2'), 6.64 (d, 4H, *J* = 8.3 Hz, OPhH–3'), 4.88 (t, 2H, *J* = 5.6 Hz, (CH_2)OH, 4.73 (dd, 2H, *J* = 7.6; 13.0 Hz, *CH), 3.64–3.49 (m, 4H, CH_2(OH)); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.74 (CO), 156.53 (OPhC–4'), 130.58 (OPhC–1'), 128.22 (OPhC–2'), 115.00 (OPhC–3'), 64.15 (CH_2OH), 55.27 (*CH).

Anal. Calcd. for $C_{18}H_{20}N_2O_6$ (M_r = 360.356): C 60.00, H 5.60, N 7.78 %; found: C 59.86, H 5.86, N 7.63 %.

(S,S) N,N'-*Bis[2-hydroxy-1-(4-hydroxybenzyl)ethyl]-ethanediamide (**4c**)*

From **4a**: 95 %; R_F *ca.* 0.6 (CH_2Cl_2:MeOH 8:2); m.p. 251–253 °C (from MeOH); $[\alpha]_D^{20}$= –56 (*c* = 1.0 g/100 ml, MeOH); IR (KBr) $\nu_{max.}$/cm^{-1}: 3449, 3381, 3293, 1654, 1508; ^{1}H NMR (DMSO-d_6) δ/ppm: 9.13 (s, 2H, D_2O exchangeable, OH–(Ph)), 8.24 (d, 2H, *J* = 9.0 Hz, D_2O exchangeable, NH), 6.92 (d, 4H, *J* = 8.3 Hz, OPhH–2'), 6.62 (d, 4H, *J* = 8.0 Hz, OPhH–3'), 4.79 (t, 2H, *J* = 5.6 Hz, D_2O exchangeable, (CH_2)OH), 3.82 (m, 2H, *CH), 3.32 (s, 4H, CH_2(OH)), 2.68 and 2.57 (dd, 2H, *J* = 5.6; 14.0 Hz, (HO)–CHa(Hb) and dd, 2H, *J* = 8.3; 14.0 Hz, (HO)–C(Ha)Hb)); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.59 (CO), 155.65 (OPhC–4'), 129.99 (OPhC–2'), 128.87 (OPhC–1'), 115.10 (OPhC–3'), 53.40 (*CH), 35.42 ((*CH)CH_2).

Anal. Calcd. for $C_{20}H_{24}N_2O_6$ (M_r = 388.408): $[M+H]^+$ = 389.170714, found $[M+H]^+$ = 389.170117.

(S,S) N,N'-*Bis{2-acetyloxy-1-[4-(benzyloxy)benzyl]-ethyl}ethanediamide (**4d**)*

A solution of benzyloxytyrosinol **4a** (300 mg, 0.58 mmol) and freshly distilled acetic anhydride (0.5 ml) in anhydrous pyridine (10 ml) was stirred at room temperature for 16 h. The solvent was evaporated under reduced pressure, traces of pyridine were removed by coevaporation with toluene (2 × 5 ml) and the residue was separated by preparative t.l.c. (two developments in CH_2Cl_2:MeOH 98:2) giving the title compound **4d** (340 mg, 90 %), R_F *ca.* 0.2 (CH_2Cl_2:MeOH 99:1), m.p. 194–195 °C (from CH_2Cl_2–Et_2O–n-hexane), $[\alpha]_D^{20}$ = –30 (*c* = 1.0 g/100 ml, CH_2Cl_2). IR (KBr) $\nu_{max.}$/cm^{-1}: 3451, 3300, 1733, 1657, 1610, 1511; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.62 (d, 2H, *J* = 8.7 Hz, NH), 7.39–7.27 (m, 10H, (CH_2)PhH), 7.05 (d, 4H, *J* = 8.1 Hz, OPhH–2'), 6.86 (d, 4H, *J* = 8.1 Hz, OPhH–3'), 4.99 (s, 4H, OCH_2(Ph)), 4.18–4.10 (m, 2H, *CH), 4.06 and 3.96 (dd, 2H, *J* = 4.2; 11.1 Hz, (HO)CHa(Hb) and dd, 2H, *J* = 7.5; 11.1 Hz, (HO)C(Ha)Hb), 2.72–2.70 (m, 4H, (*CH)CH_2), 1.93 (s, 6H, CH_3); ^{13}C NMR (DMSO-d_6) δ/ppm: 170.27 (CO, acetyl), 159.67 (CO, oxalyl), 156.92 (OPhC–4'), 137.15 (1C, (OCH_2)Ph), 130.01 (OPhC–1'), 129.98 (OPhC–2'), 128.42, 127.81, 127.69 (5CH, (OCH_2)Ph), 114.55 (OPhC–3'), 69.21 ((*CH)CH_2O), 64.76 (OCH_2(Ph)), 49.98 (*CH), 35.25 ((*CH)CH_2(Ph)), 20.61 (CH_3).

Anal. Calcd. for $C_{38}H_{40}N_2O_8$ (M_r = 652.716): C 69.92, H 6.18, N 4.29 %; found: C 69.61, H 6.24, N 4.23 %.

(S,S) N,N'-*Bis{2-benzoyloxy-1-[4-(benzyloxy)benzyl]-ethyl}ethanediamide (**4e**)*

To a solution of benzyloxytyrosinol **4a** (300 mg, 0.58 mmol) in freshly distilled and at 0 °C cooled pyridine (10 ml), benzoylchloride (0.2 ml, 1.74 mmol) was added and then stirred at 3–5 °C for 16 h. The mixture was evaporated to dryness and traces of pyridine were removed by coevaporation with toluene (2 × 5 ml). The residue was purified by preparative t.l.c. (two developments in CH_2Cl_2:MeOH 99:1) to give product **4e** (400 mg, 89 %), R_F *ca.* 0.4 (CH_2Cl_2:MeOH 99:1), m.p. 238–239 °C (from CH_2Cl_2–Et_2O–n-hexane), $[\alpha]_D^{20}$ = –25 (*c* = 1.0 g/100 ml, CH_2Cl_2). IR (KBr) $\nu_{max.}$/cm^{-1}: 3425, 3289, 1721, 1651, 1607, 1512; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.80 (d, 2H, *J* = 9.0 Hz, NH), 7.39–7.27 (m, 10H, CO–Ph), 7.05 (d, 4H, *J* = 8.1 Hz, OPhH–2'), 6.86 (d, 4H, *J* = 8.1 Hz, OPhH–3'), 4.99 (s, 4H, OCH_2(Ph)), 4.18–4.10 (m, 2H, *CH), 4.06 and 3.96 (dd, 2H, *J* = 4.2; 11.1 Hz, OCHa(Hb)(*CH) and dd, 2H, *J* = 7.5; 11.1 Hz, OC(Ha)Hb(*CH)), 2.72–2.70 (m, 4H, (*CH)CH_2); ^{13}C NMR (DMSO-d_6) δ/ppm: 165.52 (CO(Ph)), 159.86 (CONH), 156.95 (OPhC–4'), 137.14 and 128.36, 127.74, 127.61 (1C and 5CH, (CH_2)Ph), 130.10 (OPhC–1'), 129.95 (OPhC–2'), 129.45 and 133.14, 129.11, 128.48, (1C and 5CH, (CO)Ph), 114.60 (OPhC–3'), 69.24 ((*CH)CH_2O), 65.89 (OCH_2(Ph)), 49.94 (*CH), 35.07 ((*CH)CH_2(Ph)).

Anal. Calcd. for $C_{48}H_{44}N_2O_8$ (M_r = 776.848): C 74.21, H 5.71, N 3.61 %; found: C 74.36, H 5.78, N 3.58 %.

*General Procedure for the Preparation of Oxalyl-dihydroxy-diamides **4f–4h***

To a suspension of bis(tyrosinol) oxalyl amide **4c** (1 mmol) in acetonitrile (20 ml), K_2CO_3 (6 mmol) and the corresponding 1- or 2-bromomethylnaphtalenes or 4-bromomethylbiphenyl (1.1 mmol) were added. The mixture was heated to reflux for 5 h. After cooling to room temperature, the precipitate was filtrated off and washed thoroughly with water (5 x 5 ml) to remove inorganic salts. The undissolved material was air-dried, giving crystalline products **4f**, **4g** or **4h**.

(S,S) N,N'-*Bis{ 2-hydroxy-1-[4-(1-naphtylmethoxy)-benzyl]ethyl}ethanediamide (**4f**)*

From 1-bromomethylnaphtalene: 81 %; R_F *ca*. 0.45 (CH_2Cl_2: MeOH 9:1); m.p. 186–188 °C; $[\alpha]_D^{20}$ = –36 (*c* = 0.5 g/100 ml, THF); IR (KBr) ν_{max}/cm^{-1}: 3387, 3300, 1656, 1613, 1579, 1506; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.35 (d, 2H, *J* = 8.6 Hz, D_2O exchangeable, NH), 7.99–7.38 (m, 14H, 1-naphthyl), 7.09 (d, 4H, *J* = 7.6 Hz, OPhH–2'), 6.94 (d, 4H, *J* = 7.6 Hz, OPhH–3'), 5.39 (s, 4H, OCH_2(Ph)), 4.86 (br s, 2H, D_2O exchangeable, OH), 3.90 (m, 2H, *CH), 3.35 (m, 4H, CH_2(OH)), 2.72 (m, 4H, (*CH)CH_2(Ph)); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.66 (CO), 156.92 (OPhC–4'), 131.16 (OPhC–1'), 130.12 (OPhC–2'), 133.35, 132.67, 131.23, 128.71, 128.54, 126.72, 126.47, 126.01, 125.43 and 123.97 (3C and 7CH, 1-naphtyl), 114.59 (OPhC–3'), 67.82 (OCH_2(Ph)), 62.29 (CH_2OH), 53.30 (*CH), 35.35 ((*CH)CH_2(Ph)).

Compound **4f** was analyzed as diacetyl derivative. *Anal.* Calcd. for $C_{46}H_{44}N_2O_8$ x ½ H_2O (M_r = 761.836): C 72.52, H 5.95, N 3.68 %, found: C 72.68, H 6.24, N 3.54 %.

(S,S) N,N'-*Bis{ 2-hydroxy-1-[4-(2-naphtylmethoxy)-benzyl]ethyl}ethanediamide (**4g**)*

From 2-bromomethylnaphtalene: 73 %; R_F *ca*. 0.40 (CH_2Cl_2: MeOH 9:1); m.p. 211–213 °C; $[\alpha]_D^{20}$ = –26 (*c* = 0.5 g/100 ml, THF); IR (KBr) ν_{max}/cm^{-1}: 3370, 3279, 1648, 1609, 1580, 1512; ^{1}H NMR (DMSO-d_6) δ/ppm: 8.32 (d, 2H, *J* = 9.0 Hz, D_2O exchangeable, NH), 7.88–7.45 (m, 14H, 2-naphthyl), 7.056 (d, 4H, *J* = 8.6 Hz, OPhH–2'), 6.91 (d, 4H, *J* = 8.6 Hz, OPhH–3'), 5.16 (s, 4H, OCH_2(Ph)), 4.92 (br s, 2H, D_2O exchangeable, OH), 3.87 (m, 2H, *CH), 3.34 (m, 4H, –H_2(OH)), 2.76 and 2.62 (dd, 2H, *J* = 5.0; 14.0 Hz,, (HO)–CHa(Hb) and dd, 2H, *J* = 8.6; 14.0 Hz, (HO)C(Ha)Hb); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.49 (CO), 156.80 (OPhC–4'), 130.97 (OPhC–1'), 129.98 (OPhC–2'), 134.83, 132.77, 132.51, 127.97, 127.71, 127.55, 126.23, 126.14, 126.03 and 125.64 (3C and 7CH, 2-naphtyl), 114.57 (OPhC–3'), 69.37 (OCH_2(Ph)), 62.11 (CH_2OH), 53.09 (*CH), 35.27 (CH_2(*CH)).

Compound **4g** was analyzed as diacetyl derivative. *Anal.* Calcd. for $C_{46}H_{44}N_2O_8$ (M_r = 752.828): C 73.39, H 5.89, N 3.72 %, found: C 73.14, H 6.17, N 3.46 %.

(S,S) N,N'-*Bis{ 1-[4-(biphenyl-4'-ylmethoxy)benzyl]-2-hydroxyethyl}ethanediamide (**4h**)*

From 4-bromomethylbiphenyl*:* 84 %, R_F *ca*. 0.33 (CH_2Cl_2: MeOH 9:1); m.p. 244–247 °C; $[\alpha]_D^{20}$ = –31 (*c* = 1.0 g/100 ml, DMSO); IR (KBr) ν_{max}/cm^{-1}: 3378, 3279, 1656, 1608, 1581, 1506, ^{1}H NMR (DMSO-d_6) δ/ppm: 8.36 (d, 2H, *J* = 9.3 Hz, NH), 7.70–7.40 (m, 18H, biphenyl), 7.10 (d, 4H, *J* = 8.3 Hz, OPhH–2'), 6.92 (d, 4H, *J* = 8.3 Hz, OPhH–3'), 5.08 (s, 4H, OCH_2(Ph)), 3.92 (m, 6H, CH_2OH), 3.45 (m, 2H, *CH), 2.82 and 2.68 (dd, 2H, *J* = 5.0; 14.0 Hz, (HO)CHa(Hb) and dd, 2H, *J* = 8.6; 14.0 Hz, (HO)C(Ha)Hb); ^{13}C NMR (DMSO-d_6) δ/ppm: 159.59 (CO), 156.80 (OPhC–4'), 131.04 (OPhC–1'), 130.09 (OPhC–2'), 139.88, 139.71, 136.46, 129.02, 128.37, 127.57, 126.77 and 126.72 (3C and 9CH, 4-biphenyl), 114.52 (OPhC–3'), 68.91 (OCH_2(Ph)), 62.32 (CH_2OH), 53.23 (*CH), 35.30 (CH_2(*CH)).

Compound **4h** was analyzed as diacetyl derivative. *Anal.* Calcd. for $C_{50}H_{48}N_2O_8$ (M_r = 804.935): C 74.80, H 6.01, N 3.48 %; found: C 74.53, H 6.18, N 3.40 %.

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SAŽETAK

Kiralni bis(tirozinol) i bis(*p*-hidroksifenilglicinol) oksalamidni gelatori. Utjecaj aromatičkih skupina i vodikovih veza na svojstva geliranja

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Pripravljeni su enantiomerno čisti *R,R*-bis(4-hidroksifenilglicinol) oksalamidi **3** i *S,S*-bis(tirozinol) oksalamidi **4** te su ispitana njihova svojstva geliranja organskih otapala, vode i vodenih smjesa s polarnim organskim otapalima. Nađeno je da su oksalamidni spojevi s fenolnim hidroksilnim skupinama supstituiranima arilom djelotvorni organogelatori jako polarnih sustava otapala dok derivati sa slobodnim fenolnim hidroksilnim skupinama teže kristalizaciji. Ustanovljena razlika u ponašanju objašnjena je na temelju specifičnih vodikovih veza nađenih u kristalnoj strukturi.