



Synthesis and fluorescent properties of novel chiral 1,2-diaminocyclohexane substituted ligands and their complexes



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ABSTRACT

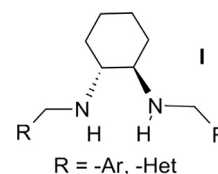
A series of novel chiral 1,2-diaminocyclohexane derivatives bearing heterocyclic units were synthesized via improved methods under ultrasonic irradiation. The photophysical properties of compounds were studied in ethanol, methanol, and chloroform. The sensitivity of these amines toward Cu^{2+} , Cd^{2+} , and Ni^{2+} was studied by the UV–vis and fluorescent methods. The π -electron structure of thiophene and bithiophene containing sensors is the most active toward all above mentioned metal ions and is highly selective for Ni^{2+} and Cd^{2+} .

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1. Introduction

Fluorescent compounds represent an important type of organic compounds due to their properties and variety of applications with strong potential as photochromic azo dyes, chromophores, and in vitro fluorescent imaging probes for biondiagnosis.^{1–5} Push–pull substituted heterocyclic compounds are of great interest due to their non-linear optical properties, which are useful for optoelectronic devices.^{6,7} Fluorophores based on a bithiophene structure are used in excitation chirality method for determining the absolute configurations of chiral molecules on a microscale level and the recognition of chiral molecules.^{8,9} In recent years, the research work of chemical sensors for ions began to develop rapidly and to replace traditional analytical methods due to their advantages such as high sensitivity, selectivity, and detection simplicity.¹⁰ The chiral recognition method involves the application of chiral structures with optical properties. The structure of non-racemic *trans*-1,2-diaminocyclohexane satisfies requirements mentioned above. Thus new chiral sensors for ions and biomolecules based on the 1,2-diaminocyclohexane moiety have become a fast-growing research field.^{8,11–14} Fluorescent receptors based on 1,2-diaminocyclohexane with thiophene units indicate good results for recognition of fluoride ions.¹⁵ Three decades ago, asymmetric

reactions began to play an important role in modern organic synthesis.^{16–18} The synthesis of new chiral ligands in asymmetric reactions is the subject of ongoing scientific research.^{16–18} Complexes based on chiral 1,2-diaminocyclohexane with aromatic fragments are widely used in some asymmetric reactions: epoxidation of alkenes,¹⁹ asymmetric allylic alkylation,²⁰ Henry reaction, and Michael addition.^{17,18,21} It has been shown that the properties of metal complexes depend on the structure and metal-specific binding site of the ligand.²² The chiral unit of 1,2-diaminocyclohexane has the most suitable geometry parameters and commercial availability therefore it is the one of the important parts of the ligand structure.^{23,24} It is found that thiophene containing ligands (**I**) have very good coordinating ability therefore vacant transition metal orbitals and π -rich heteroatoms of the thiophene fragment are involved in complex formation.¹⁸ Suitable catalysts, such as complexes of **I** $\text{Cu}(\text{II})$, have been found to greatly increase enantioselectivity in the Henry reaction.¹⁸



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High enantioselectivity and good yields made this research field ripe for further exploration, and a series of thiophene containing

ligands were synthesized.^{23,25} The best results in allylic alkylation were obtained by using palladium complexes with two or three thiophene units in the coordination sphere of the ligand structure.^{23,26} Synthesis, catalytic activity, and spectroscopic properties of thiophene, furan ligands and their derivatives, especially the nickel complexes, have been insufficiently studied.^{21,27} In addition, the development of chiral ligands allows them to be used as highly sensitive, selective, and effective metal ion sensors and opens a wide spectrum for their application.^{10,13}

To research optical properties and the potential applications, a series of new heterocyclic chiral structures based on 1,2-diaminocyclohexane were synthesized in this work. The aim of this work was the synthesis of a series of heterocyclic ligands based on 1,2-diaminocyclohexane as a chiral unit, and to study and compare optical properties of ligands and their metal complexes.

2. Results and discussion

2.1. Chemistry

In recent years several methods for the synthesis of chiral ligands based on 1,2-diaminocyclohexane have been reported. One of the methods for azomethine synthesis from the free (*R,R*)-1,2-diaminocyclohexane and aromatic aldehydes was carried out in dichloromethane or ethanol as solvent in the presence of anhydrous magnesium sulfate for 32 h at ambient temperature.^{11,22,23,31–33} Significant improvement in some experiments was achieved using of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (DACHT) to avoid the use of water-soluble air-sensitive free diamine in the reaction and the use of water-removing reagents (MgSO₄, Na₂SO₄, molecular sieves).^{11,23,28,29,32} Thereby the reaction time was decreased and the requirement to change reaction conditions depending on the aldehyde structure was excluded.^{11,23,28,29,32} However, for isolation of free diamine from DACHT, base is required.²⁹ Condensation of aromatic aldehydes with DACHT at reflux in water/ethanol mixture in presence of potassium carbonate produced azomethines with good yields.^{23,30} New methods for reaction stimulation such as microwave and ultrasonic irradiation may facilitate some reactions.²⁴ The most studied heterocyclic diimines and their complexes are based on thiophene-2-carbaldehyde, however, there are no data about thiophene-3-carbaldehyde and a lack information about furan ligands, their complexes, and spectroscopic properties.

It should be mentioned that carrying out the experiment under the described conditions³⁰ with increase of the reaction temperature but without ultrasonic irradiation gives low yields and side products. Ultrasonic irradiation of reaction media is a useful method for preparation a series of azomethines (**3a–3f**) from corresponding aldehydes (**2a–2f**) and (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (Scheme 1).

The use of ultrasonic irradiation for reaction activation allowed the reaction time to be reduced to 1 h and the diimines to be isolated in good yields. However, the reaction time and yield are seen to be greatly affected by the absence of ultrasonic irradiation. The most suitable molar ratio of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt/aromatic aldehyde/potassium carbonate is 1:2:2, respectively.

Our interest is focused on the further reduction of the azomethines (**2a–2f**) to obtain new heterocyclic ligands for complex formation with potential uses in asymmetric catalysis. Reduction of the C=N bond in azomethines use NaBH₄/methanol or NaBH₄/THF with 10-fold excess of NaBH₄ and the reaction time varies up to 16 h at room temperature with good yields,^{11,22,23,29,34,35} but described reaction conditions lead to low yields of amines with heterocyclic fragments. We found the reaction can be carried out in ethanol with NaBH₄ with reflux for 1 h of the reaction mixture. The corresponding chiral amines (**3a–3f**) were obtained with high yields (>90%) (Scheme 2).

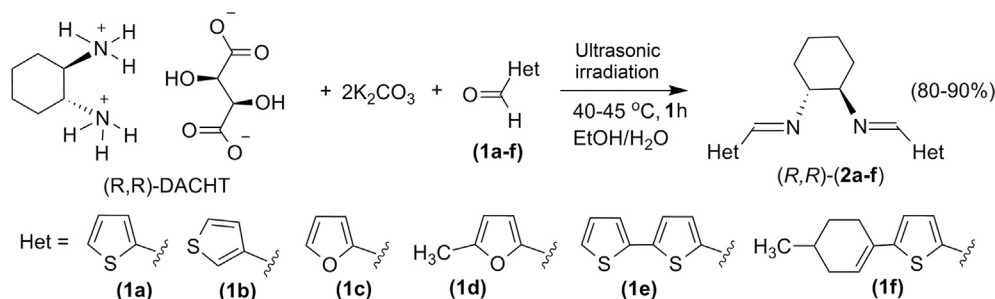
The most suitable molar ratio of azomethine/NaBH₄ is 1:2:2, respectively, and the minimum volume of ethanol was used in the reaction.

2.2. Spectroscopic properties

The electronic spectra of compounds (**3a–3f**) were recorded in chloroform (10⁻³ M) and showed an intense lowest energy charge-transfer absorption band in the UV-region (Table 1). All compounds (**3a–3f**) exhibit an intense absorption in the UV-region and the position of this band depends on the electronic nature of the heterocyclic ring and ring substituent.

A slight bathochromic shift (8 nm) in the absorption spectrum in chloroform was observed for structure **3a** in comparison with **3b** that proves greater interaction of the α -substituent with thiophene π -system in **3a** (Table 1). There is no significant effect on the absorption maxima of compound **3c** with a furan moiety in comparison with **3a**. At the same time, there is a slight bathochromic shift (8 nm) for the methylfuran structure (**3d**). The most considerable red-shift was observed for the 2,2'-bithiophene structure (**3e**) and, as with compound **3f**, it may suggest an interaction of the two π -electronic systems: thiophene and olefin moieties. The absorption spectrum of 2,2'-bithiophene containing structure (**3e**) shows two main absorption bands in chloroform (Table 1). A broad band at ca. 355 nm may be ascribed to an electron transfer transition and a band of moderate intensity at ca. 250 nm may represent the π - π^* local excitation transition of the heteroaromatic ring.

We measured the emission characteristics of compounds **3a–3f** in chloroform. All the emission spectra have a wide contour. In spite of the similar absorption maxima for **3a** and **3b**, two fluorescence maxima were observed for 3-thienyl substituted 1,2-diaminocyclohexane (**3b**). It is unexpected that the most significant bathochromic shift was noticed for the bis(2-furfuryl)



Scheme 1. Synthesis of diimines (**2a–2f**).

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