(-)-(*R,R*)-*N,N′*-Bis(3-nitro-salicylidene)-1,2-cyclohexanediamine as a new host compound for aromatic guests through CH/Л interactions

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Dedicated to Professor Alexandru Balaban
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Abstract
Optically pure *N,N′*-bis(3-nitro-salicylidene)-1,2-cyclohexanediamine formed inclusion complex crystals with aromatic guest molecules (toluene, p-xylene, aniline), whereas the *racemic* or *meso* forms crystallized without inclusion of these guests. The guest aromatic rings are sandwiched by two host molecules involving the axial CH bonds of the cyclohexyl group to develop CH/Л interactions. *p*-Xylene was selectively extracted from the mixture of isomeric xylenes.

Keywords: Inclusion complexes, CH/Л interaction, clathrate

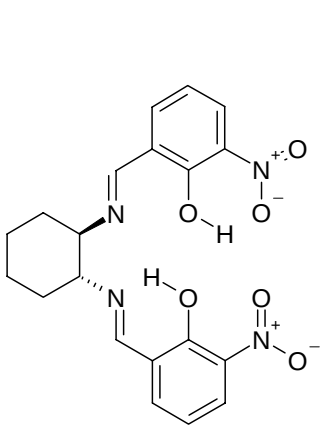
Introduction

Many examples of inclusion of aromatic guests in crystals are known in the literature, л-л stacking and hydrogen bonding (for benzene, phenols, phenylenediamines, tropolone) are generally involved.[1] The importance of CH/Л hydrogen bonds in crystals have been recently reviewed by M. Nishio.[2] We were interested in the likely stacking of an aromatic ring with a cyclohexane group through 3 CH/Л hydrogen bonds involving the 3 axial CH bonds. Toda et al. reported that bis(hydroxydiphenylmethyl)cyclohexane formed a crystal complex with benzene in a host-guest ratio 2:1. Unfortunately a single crystal suitable for X-ray analysis was not obtained to observe the relative arrangement of the benzene and cyclohexane.[3] Jones et al. observed the formation of a solvate between toluene and *rac*-N,N′-bis(4-dimethylaminobenzylidene)-1,2-diaminocyclohexane and provided the crystal data.[4] However, the X-ray files are no longer available from the authors and thus the relative positions of the toluene and cyclohexane groups are not available in this clathrate.[5] We observed that some bis-salicylidene-1,2-

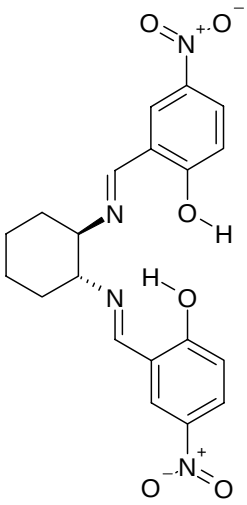
cyclohexanediamine derivatives formed stable crystals with aromatic solvents and we report herein the results of our observations.

Results and Discussion

The bis-imines resulting from the reaction of salicylaldehyde derivatives with enantiomerically pure 1,2-diaminocyclohexane are well known for their liganding properties to metals yielding chiral metal salen Schiff-base catalysts. These chiral catalysts proved very efficient in various asymmetric reactions pioneered by Jacobsen's and Katsuki's groups.[6] We were interested in the enantioselective complexing abilities of metal-free optically pure bis-imines and thus several derivatives were prepared by conventional synthesis.[7,8] Our interest was mainly focused on compounds having a nitro group in the 3- or 5- position of the aromatic ring in order to increase the hydrogen bonding ability of the phenol. Thus, new (-)-(R,R)-N,N′-bis(3-nitro-salicylidene)-1,2-cyclohexanediamine (R,R)-**1** and the already described[8] 5-nitro analogue (R,R)-**2** were obtained under various classical experimental conditions using CH_2Cl_2 or water/EtOH mixtures.[7,8]



(R,R)-**1**



(R,R)-**2**

Scheme 1. Structures of (R,R)-**1** and (R,R)-**2**.

These conditions afforded orange-yellow solids, the analyses of which were consistent with the expected structures. We tried azeotropic elimination of water by toluene to improve the reaction conditions. Under these conditions a nice yellow crystalline compound (mp = 110°C) was obtained during the synthesis of (R,R)-**1**. These crystals were dried under vacuum for a period of 1 hour at 3 torr without alteration. The NMR spectra of the crystals dissolved in $CHCl_3$ showed the presence of toluene and (R,R)-**1** in a 1:1 ratio. The same crystals (mp = 110°C) were

obtained after dissolution of powdered (R,R)-**1** in hot methyl acetate upon addition of toluene and slow evaporation of the solvent. Clearly a 1:1 inclusion complex is formed between toluene (guest) and (R,R)-**1** (host). NMR analysis showed that the 5-nitro derivative (R,R)-**2** crystallized without toluene inclusion.

X-ray single crystal analysis confirmed the host-guest relationship between (R,R)-**1** and toluene. (Figure 1). Interestingly, the toluene was located on the cyclohexane ring exhibiting CH/Л interactions instead of the likely Л stacking with the nitrophenol (face-face or front-edge). Furthermore a disorder in the orientation of the toluene was observed pointing out that the crystal might accommodate p-xylene.

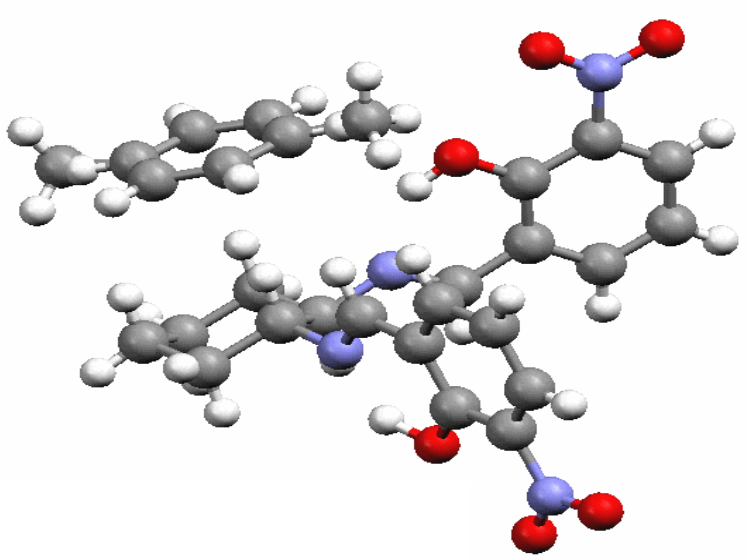


Figure 1. X-ray of the complex formed between toluene and (R,R)-**1** (note: toluene presents a disorder).

(R,R)-**1** and (R,R)-**2** were dissolved in methyl acetate in two different flasks. Addition of p-xylene in both flasks, at room-temperature, resulted after a few seconds in an abundant crystallisation (long yellow needles mp = 130°C) in the flask containing (R,R)-**1** whereas the flask containing (R,R)-**2** remained unchanged during the same period of time. Solution NMR of the isolated crystals showed that, in the clathrate, the p-xylene was included in a 1:1 guest-host ratio. X-ray single crystal analysis[†] showed that, here again, the p-xylene guest molecule was situated on the cyclohexane framework developing CH/Л interactions with the axial hydrogens (Figure 2).

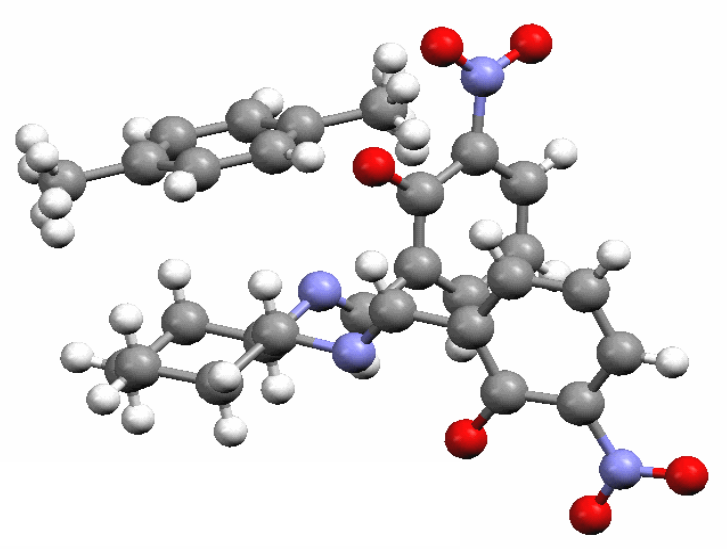


Figure 2. X-ray of the complex formed between p-xylene and (R,R)-**1**.

In another experiment, (R,R)-**1** was added to an equimolecular mixture of the three isomeric xylenes in a molar ratio of 1/18, and analysis of the resulting crystals by solution NMR showed that p-xylene was included in the crystal with a high selectivity (> 96%), indicating a noteworthy shape discriminating ability towards isomeric xylenes. Further GLC analysis showed that m-xylene was not taken-up in the crystal and the remaining 4% were composed of o-xylene. The selectivity might be improved with further optimization of the crystallization process. A single precedent for the preferential uptake of the p-xylene with comparable selectivity has been reported using $Ph_2P(Se)C_2H_4P(Se)Ph_2$.[9]

(R,R)-**1** also formed host-guest inclusion crystal with aniline (yellow crystals mp = 134-136°C). Single crystal analysis[†] showed that aniline is also standing on the cyclohexane moiety as it was for toluene or p-xylene (Figure 3). Hydrogen bonding with one phenol group eliminated the disorder which was observed for toluene.

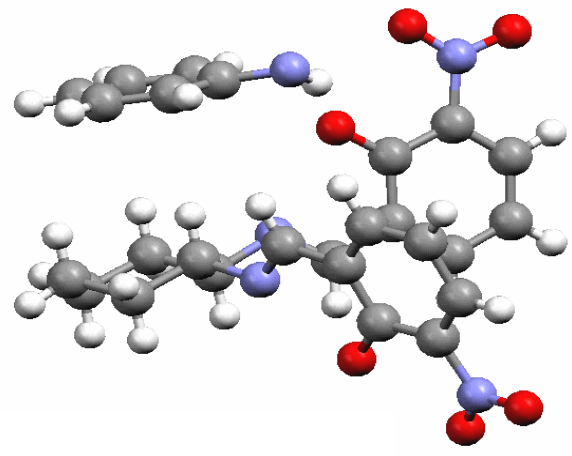


Figure 3. X-ray of the complex formed between aniline and (R,R)-**1**.

Thus, we have revealed a new host compound which selectively produced clathrates with aromatic derivatives. Interestingly, the aromatic guests are standing in all cases on the cyclohexane framework developing CH/Л interactions.[2,10] The distances between the mean plane of the guest aromatic ring, defined by all non-hydrogen atoms, and the three axially pointing C-H's of the cyclohexane ring are 2.908, 2.854 and 2.838 Å for the complex formed with toluene, 2.864, 2.864 and 2.829 Å for the complex formed with p-xylene and 2.842, 2.804 and 2.774 Å for the complex formed with aniline. These distances are in the usual range for CH/Л interactions.

Optically pure (R,R)-**1** formed crystalline inclusion complexes with aromatics, and it was inviting to investigate whether *rac*-**1** or *meso*-**1** would behave similarly. *Rac*-**1** or *meso*-**1** did not form inclusion crystal complexes with the aromatic guests previously described as shown by solution NMR of the crystals.

(R,R)-**1** being optically pure, a preliminary assay to discriminate between enantiomers was performed on *rac*-1-phenyl-ethan-1-ol without success: no inclusion of the alcohol occurred.

Conclusions

CH/Л interactions are involved in the formation of 1:1 clathrates between an aromatic guest and a cyclohexane-derived host.

A large diversity of substituents is available on the key framework of salicylaldehyde,[11] thus a fairly large library of *N,N'*-bis-salicylidene-1,2-cyclohexanediamine derivatives can be prepared in high yields. The fact that the starting 1,2-diaminocyclohexane is available in racemic, meso or optically pure forms greatly enhances the field of investigation for further selective and (or) enantioselective host-guest studies.

Experimental Section

General Procedures. Melting points were taken using a Kofler plate and are uncorrected. Optical rotations were measured on a Perkin Elmer MC241 digital polarimeter with a cuvette of 1 cm length. Specific rotations ($[\alpha]_D$) are reported in degrees per decimeter at room temperature, and the concentration (*c*) is given in grams per 100 mL in the specified solvent. Elemental analyses were performed either at Service Central d'Analyse (CNRS) and Inter-University Research Facility of Marseille. ^{1}H-NMR spectra were recorded at 200 or 300 MHz with TMS as the internal standard or $CHCl_3$ (δ_H 7.26); ^{13}C-NMR were recorded at 50 or 75 MHz with $CDCl_3$ (δ_C 77.1 (central line of t)) as the internal standard. NMR were recorded Bruker AC-200 or AC-300 at the Inter-University Research Facility of Marseilles "Centre Régional de RMN". Mass spectra were determined on a JEOL MR SX102 mass spectrometer using FAB technique with matrix NBA. Commercial solvents such as CH_2Cl_2 or absolute ethanol were used without further purification.

Compound characterization

(1*R*,2*R*)-*N*,*N*′-Bis(3-nitro-salicylidene)-1,2-cyclohexanediamine ((R,R)-1)

Method 1. A 250-mL, three-necked, round bottomed flask equipped with a reverse Dean Stark trap for solvent heavier than water, a pressure-equalizing addition funnel, a thermometer, a Teflon coated magnetic stirrer bar and an argon inlet was assembled and flushed with a stream of argon. A solution of (1R,2R)-(-)-*trans*-1,2-diaminocyclohexane (0.57 g, 5 mmol) in 20 mL dichloromethane was added to the flask. 3-Nitrosalicylaldehyde (1.75 g, 10.5 mmol) was dissolved in 30 mL of dichloromethane and placed in the addition funnel. The argon inlet is removed and the solution of aldehyde was added to the stirred solution of diamine over 15 minutes. An exothermic reaction occurs; the reaction mixture was gently heated upon complete disappearance of water-dichloromethane azeotrope. The resulting mixture then was allowed to cool slowly to room temperature and stirred for 15 min. During concentration and cooling period an orange yellow solid precipitated. Evaporation of solvent afforded the crude **(**1*R*,2*R*)-*N,N*′-bis(3-nitro-salicylidene)-1,2-cyclohexanediamine **((R,R)-1**) as an orange viscous liquid which upon further drying afforded a powder in nearly 100% yield with trace of excess 3-nitrosalicylaldehyde. The crude product was refluxed with 20 mL of absolute ethanol, cooled, filtered and vacuum dried to afford (R,R)-**1** as an orange yellow solid in 82% yield (1.7 g, 4.1 mmol). mp 90-94°C & then 124-126°C; $[\alpha]^{25}_D$ = -919 (c=0.49, $CHCl_3$); IR (KBr, cm^{-1}) 3446, 2929, 2852, 1636, 1523; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 15.34 (2H, b), 8.33 (2H, s), 8.03 (2H, dd, *J* = 1.7, 8.3 Hz), 7.43 (2H, dd, *J* = 1.7, 7.6 Hz), 6.83 (2H,t, *J* = 7.9 Hz), 3.44 (2H,m), 2.1-1.4 (8H, m); ^{13}C-NMR δ 164.7, 158.6, 138.3, 137.5, 130.0, 120.3, 116.9, 71.4, 32.9, 24.0; Anal. Calcd for $C_{20}H_{20}N_4O_6$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.19; H, 5.07; N, 13.34. MS, *m/z*: 413 (MH^+, 100%), 397 (30%), 367 (10%).

Method 2. The general procedure described by Jacobsen et al[7] or Zheng et al.[8] with modification at the last extraction step was applied. A 500-mL, three necked flask equipped with a mechanical

stirrer, a reflux condenser, a thermometer, and an addition funnel was charged with 1,2-diammoniumcyclohexane monotartrate salt (1.32 g, 5 mmol), K_2CO_3 (1.38 g, 10 mmol), and distilled water (25 mL). The mixture was stirred until dissolution was achieved, and then ordinary ethanol (100 mL) was added. The resulting mixture was heated to reflux, and a solution of 3-nitrosalicylaldehyde in absolute ethanol (1.75 g, 10.5 mmol in 50 mL) was added over a period of 10 minutes. The funnel was rinsed with absolute ethanol (5 mL), and the yellow slurry was stirred at reflux for 2 hours. Water (20 mL) was added & the stirred mixture was cooled to 0°C, and the temperature was maintained below 5°C for 2 hours. Ethanol was evaporated and the mixture was carefully neutralized with a solution of hydrochloric acid. An orange precipitate was obtained by adjusting the pH of the mixture to ~5. The precipitate was washed with water (40 mL) and extracted with chloroform (2x30 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and reduced to a viscous and foaming liquid which with further evaporation gave an orange powder (1.80 g, 4.4 mmol, 88%): mp 88-90 °C & then ~110 °C. This powder melted at 88-90 °C then stuck on the Kofler plate, scratching the plate gave a solid which melted at ca 110 °C.

***rac-trans-N,N′*-Bis(3-nitro-salicylidene)-1,2-cyclohexanediamine *rac*-1.** Yellow powder, mp 205–206°C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 15.32 (2H, b), 8.34 (2H, s), 8.04 (2H, dd), 7.44 (2H, dd), 6.83 (2H, t), 3.44 (2H,m), 2.1-1.4 (8H,m); ^{13}C-NMR δ 164.6, 158.6, 138.2, 137.5, 130.0, 120.2, 116.8, 71.3, 32.8, 23.9; Anal. Calcd for $C_{20}H_{20}N_4O_6$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.46; H, 4.98; N, 13.49.

***cis-N,N′*-Bis(3-nitro-salicylidene)-1,2-cyclohexanediamine *meso*-1.** Orange powder, mp 202–203°C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 15.37 (2H, b), 8.40 (2H, s), 8.07 (2H, dd), 7.51 (2H, dd), 6.87 (2H, t), 3.87 (2H,m), 2.1-1.4 (8H, m); ^{13}C-NMR δ 164.0, 158.9, 138.4, 137.6, 130.1, 120.4, 116.6, 67.0, 29.5, 22.2; Anal Calcd for $C_{20}H_{20}N_4O_6$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.36; H, 4.92; N, 13.59.

(1*R*,2*R*)-*N,N′*-Bis(5-nitro-salicylidene)-1,2-cyclohexanediamine ((R,R)-2) was obtained according to reference 8.

Formation of host: guest inclusion compounds. (R,R)-**1** (40 -50 mg) was placed in a 20 mL test tube and dissolved in hot methyl acetate (4 mL) aromatic solvent (ca 1 mL) was added. The mixture was heated and filtered in a dry 20 mL test tube. Upon slow evaporation of solvent (in case of p-xylene in few minutes) yellow to orange needles crystal precipitate. The excess of solvent was withdrawn with a capillary Pasteur pipette and the solid was washed with few drops of methyl acetate.

The solvent was rapidly withdrawn as in the previous step and the test tube was flushed with argon and dried under vacuum for a period of 1 hr at 3 torr.

Selective formation of host: guest inclusion compounds with a mixtures of *o*-, *m*- & *p*-xylene. (R,R)-**1** (82 mg, 0.20 mmol) was placed in a dry test tube and xylene isomers with a total molar ratio ca 1/18 (o-xylene: 0.384 g, m-xylene: 0.389 g and p-xylene: 0.397 g) were added. Workup and crystallization described as above afforded yellow crystals (50 mg). A sample of the resulting crystals was dissolved in methyl acetate and analyzed by gas chromatography Column:

CP-Sil 5 BPX35 (30 m x 0.25 mm ID) m- and p-xylene: 96%, o-xylene: ca 4%. ^{1}H-NMR of a sample of crystal confirms that the amount of entrapped m-xylene is negligible.

(1*R*, 2*R*)-*trans*-1,2-Diammoniumcyclohexane mono-(+)-tartrate salt. This salt was prepared according to the procedure described by Eric N. Jacobsen & al.[7] $[\alpha]^{25}_D = 12.7$ (c=1, H_2O).

(-) -(1*R*, 2*R*)-*trans*-1,2-Diaminocyclohexane. To a magnetically stirred solution of 13.2 g (0.05 mol) of (1R, 2R)-*trans*-1,2-diammoniumcyclohexane mono-(+)-tartrate salt in 40 mL water and 50 mL CH_2Cl_2 under an inert argon atmosphere was added dropwise a cooled solution of NaOH (4.8g, 0.12 mole) in 40 mL water. After addition of NaCl (3 g) the mixture was stirred for 30 minutes. After decantation and extraction of aqueous phase with dichloromethane (3x20 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated to yield a colorless oil (2.8 g, 49%) which was conserved under an inert argon atmosphere.

3-Nitrosalicylaldehyde. Salicylaldehyde was nitrated using the procedure described by Hach et al.[12] and the 3-nitro (the minor isomer) was separated from 5-nitro isomer by the method of von Miller.[13] Multiple fractional crystallization of the sodium (or potassium) salts from water afforded 3-nitrosalicylaldehyde (mp 108-109 °C).

X-Ray data. †Crystal data for clathrate (R,R)-**1**: toluene: C27 H28 N4 O6, M = 504.53, orthorhombic, a = 8.2250(4), b = 17.2550(3) , c =18.2490(7) Å, α = 90.00, β = 90.00, γ = 90.00, *U* = 2589.94(17) Å^3, *T* = 293(2) K, space group $P2_12_12_1$, *Z* = 4, μ(Mo-Kα) = 0.71073 Å, 2740 reflections measured, 2467 unique (R_{int} = 0.054). The final wR was 0.1435; for clathrate (R,R)-**1**: p-xylene: C28 H28 N4 O6, M = 516.54, orthorhombic, a = 8.2000(2), b = 17.7530(1) , c =18.1370(1) Å, α = 90.00, β = 90.00, γ = 90.00, *U* = 2640.3(2) Å^3, *T* = 293(2) K, space group *C2 2 2*$_1$, *Z* = 4, μ(Mo-Kα) = 0.71073 Å, 1401 reflections measured, 1295 unique (R_{int} = 0.054). The final wR was 0.1697; for clathrate (R,R)-**1**:aniline : C26 H25 N5 O6, M = 503.51, orthorhombic, a = 8.1000(2), b = 17.2100(7), c =18.0580(7) Å, α = 90.00, β = 90.00, γ = 90.00, *U* = 2517.30(15) Å^3, *T* = 293(2) K, space group $P2_12_12_1$, *Z* = 4, μ(Mo-Kα) = 0.71073 Å, 2642 reflections measured, 2451 unique (R_{int} = 0.049). The final wR was 0.1600. The structure have been deposited at the Cambridge Crystallographic database under the following references: clathrate (R,R)-**1**:toluene CCDC 224719; clathrate (R,R)-**1**:p-xylene CCDC 224720 and clathrate (R,R)-**1**:aniline CCDC 224721.

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