Abstract

The macrocycle in rotaxane 1 is preferentially hydrogen-bonded to the succinamide station in the neutral form, but can be moved to the naphthalimide station by one-electron reduction of the latter. The hydrogen bonding between the amide NH groups of the macrocycle and the C=O groups in the binding stations in the thread was studied with infrared spectroscopy in different solvents in both states. In addition, the solvent effect on the vibrational frequencies was analyzed; a correlation with the solvent acceptor number ($AN$) was observed. The conformational switching upon electrochemical reduction could be detected by monitoring the hydrogen-bond induced shifts of the $\nu(CO)$ frequencies of the C=O groups of the succinamide and the reduced naphthalimide stations. The macrocycle was found to shield the encapsulated station from the solvent: wavenumbers of $\nu(CO)$ bands of the C=O groups residing inside the macrocycle cavity remain unaffected by the solvent polarity.

3.1 Introduction

Exploitation of intercomponent mobility in rotaxanes and other interlocked molecular assemblies has emerged as an appealing subject of research during the past decade.\cite{1-5} The key challenge is to control the intercomponent degrees of freedom, which can be accomplished by the modulation of the weak interactions between the components. In the case of rotaxanes, changing the interactions between the macrocyclic ring and binding stations in the thread can result in reversible transitions between structurally well-defined states in which the ring binds to different parts of the thread (conformers). If this shuttling is signalled by an observable change in a physical or chemical property of the system, the molecule behaves as a switch. These molecular switches are also referred to as molecular motors, because they are in principle capable of converting chemical energy into mechanical work. Molecular switches have also been proposed to be promising candidates for key elements in molecular scale information processing devices. Interlocked systems have been designed in which hydrogen bonding,\cite{6-9} π-π-interactions,\cite{10,11} metal coordination,\cite{12,13} Coulombic forces and hydrophobic interactions,\cite{14,15} are utilized, not only to allow template-directed synthesis, but also to control the intercomponent interactions. In order to fully exploit the potential of these molecules and for the design of new molecules with improved performance, a detailed understanding of the intercomponent interactions is mandatory.

In this chapter, we describe the infrared study of hydrogen bond interactions in rotaxane 1 (Figure 3-1) containing two potential binding stations for the macrocycle: a succinamide (suc) and a naphthalimide (ni) station. The succinamide group is known to be a better hydrogen bond acceptor than the naphthalimide station. Hence, in the thermodynamically favored conformer the macrocycle resides at the succinamide station.\cite{16,17}

![Figure 3-1 Molecular structures of the studied switchable hydrogen-bonded rotaxane 1, thread 2, naphthalimide model compound 3 and succinamide model compound 4.](image)
The switching function in rotaxane 1 is based on the shuttling of the macrocycle between the two stations, which is triggered by one-electron reduction of the naphthalimide station, either electrochemically\(^{[17]}\) or photochemically\(^{[16]}\) (Scheme 3-1). The thus formed naphthalimide radical anion has a higher hydrogen bonding affinity towards the macrocycle, which results in a net translational motion of the macrocycle towards the naphthalimide radical anion to form the energetically more favorable co-conformer \(n\-1^{\ddagger}\).

The shuttling process was studied in a time-resolved way by using the electronic absorption spectrum of the naphthalimide radical anion as probe\(^{[16]}\). With this method the shuttling was revealed by monitoring the precise position of the strong electronic absorption band near 420 nm, which undergoes a blue-shift when the macrocycle binds to the radical anion.

**Scheme 3-1** Shuttling cycle of rotaxane 1 upon one-electron reduction and re-oxidation of the naphthalimide station.

An alternative approach to study the structural changes during the shuttling process is by using the macrocycle as a probe, since in contrast to the succinamide and naphthalimide stations, this component is directly involved at every stage of the process. In the course of the shuttling cycle, hydrogen bonds of the macrocycle to the succinamide station are broken, and after the shuttling new hydrogen bonds are formed with the naphthalimide radical anion. Thus, direct monitoring of hydrogen bonds during the shuttling would be an ideal way to study the process.

Infrared (IR) spectroscopy is a promising technique for this purpose. It provides structural information, and can be applied with the sub-microsecond time resolution needed to monitor the shuttling process.\(^{[18]}\) IR spectroscopy has been widely used in the analysis of
secondary structural motifs in proteins and peptides which are determined to a large extent by hydrogen bonding interactions. These studies therefore usually focus on the detection of hydrogen bonds between amide groups. The amide C=O stretching ($\nu(CO)$, often called the Amide I band) and NH stretching [$\nu(NH)$] frequencies are strongly affected by hydrogen bonds, making the amide group an exceptionally good probe for the study of hydrogen-bond stabilized conformers. Hydrogen bonding between amide groups decreases the NH and C=O bond orders in both acceptor amide and donor amide. Therefore, for amides involved in hydrogen bonding, generally a large red-shift of the $\nu(CO)$ and $\nu(NH)$ frequencies is observed.

So far, only a few reports on the application of IR spectroscopy in studies of intercomponent interactions in interlocked molecules have been published in the literature. The first one was concerned with a hydrogen-bonded [2]catenane. In particular, the characterization of amide C=O and NH vibrations in a benzylic amide [2]catenane, and the consequences of the interlocked structure for these vibrations were presented. The [2]catenane studied was an interlocked dimer of the macrocycle contained in 1. In a later work, IR spectroscopy was used to study external effects on the intercomponent hydrogen bonding in this [2]catenane incorporated in different inorganic salt matrices. The salt matrix was shown to influence the number and geometry of hydrogen bonds between the macrocycle amide groups. The only reported IR study of interlocked molecules in solution was done on a succinamide rotaxane. Two-dimensional IR spectroscopy was used to determine the conformations of this rotaxane via the dipolar interactions of the C=O groups. Hydrogen bonds in rotaxanes and the effect on the vibrational frequencies of the involved donor and acceptor groups have also been analyzed with quantum chemical calculations. Calculation of the vibrational frequencies in rotaxane mimics (hydrogen-bonded complexes of isophthalic amide donor and different acceptors) showed pronounced red-shifts of $\nu(CO)$ bands of the both the acceptor ($35 - 65 \text{ cm}^{-1}$) and the donor.

The goal of the present work is to study the nature and strength of the intercomponent hydrogen bonds in the neutral and reduced forms of rotaxane 1 and thread 2 and to investigate how these interactions are modified by medium polarity. Furthermore, we want to correlate these interactions with properties such as shuttling rate and co-conformer distribution. In addition, the solvent effect on the vibrational frequencies will be analyzed. For a detailed understanding of the relationship between spectral features and molecular conformations, the C=O stretching modes of 1 and 2 will be characterized. Additional information is obtained from an analysis of the NH stretching vibrations. The structures and energies of the co-conformers of rotaxane 1 are to a large extent determined by the formation of hydrogen bonds. Hydrogen bonding is strongly affected by the solvent polarity, being more favored in solvents of lower polarity. In order to study the effect of the solvent polarity on the hydrogen bonding in 1, IR spectra were recorded in structurally
similar non-hydrogen bonding chlorinated solvents with different dielectric constants ($\varepsilon$): chloroform (CHCl$_3$, $\varepsilon = 4.70$), dichloromethane (CH$_2$Cl$_2$, $\varepsilon = 8.93$) and 1,2-dichloroethane (ClCH$_2$CH$_2$Cl, $\varepsilon = 10.36$). Also weakly hydrogen bond accepting solvents, tetrahydrofuran (THF, $\varepsilon = 7.58$) and butyronitrile (PrCN, $\varepsilon = 27.2$) were used.

Examination of the molecular structures of 1 and 2 leads us to predict the appearance of a complex combination of IR bands originating from different $\nu$(CO) modes of C=O groups of the succinamide (succ-CO) and naphthalimide (ni-CO) stations and the macrocycle (mac-CO). In the IR spectra of the radical anions drastic changes of the $\nu$(CO) bands of the naphthalimide C=O groups ($\nu^{\mathrm{\scriptscriptstyle+n}}$(CO)) are to be expected. In order to facilitate the assignment of the bands, model compounds for the succinamide (4) and naphthalimide (3) stations were synthesized and studied (Figure 3-1). Unfortunately, the macrocycle itself could not be used in this study because of its very poor solubility in non-hydrogen bonding solvents.$^{31}$ Model compounds 3 (neutral molecule and radical anion) and 4 will be shown to allow separate assignment of the $\nu$(CO) bands in the IR spectra to different C=O groups present in the succinamide and naphthalimide moieties of 1, $1^-$, 2 and $2^-$. Also, B3LYP/6-31G(d) calculations have been performed to predict the nature and frequencies of the vibrational modes and further support the spectral analysis.

3.2 Results and Discussion

3.2.1 Amide I

An overview of the different $\nu$(CO) bands expected in the IR spectra of 1 – 4 is given in Figure 3-2. Due to the procedure for sample preparation, the concentration of each solution, and therefore the molar absorption coefficients, were known only approximately.

![Figure 3-2](image)

**Figure 3-2** The different $\nu$(CO) bands of C=O groups in the succinamide and naphthalimide units and the macrocycle. The intramolecularly hydrogen-bonded conformations of the succinamide station (4a and 4b, see Figure 3-4) are not included in this overview.

In order to allow comparison of the IR bands of the different compounds, all spectra were scaled to the intensity of naphthalimide symmetric C=O stretching [$\nu_{\mathrm{\scriptscriptstyle s}}$(CO)$_{\mathrm{mac}}$] band at
ca. 1700 cm\(^{-1}\). This \(\nu(CO)\) band was chosen as a standard for two reasons: this C=O group was found to be free of interactions with other parts of the molecule and the corresponding \(\nu(CO)\) band is well separated from the other bands. The absorption coefficient of the \(\nu(CO)\) band at ~1700 cm\(^{-1}\) is \((6 \pm 2) \times 10^2\) L mol\(^{-1}\) cm\(^{-1}\).

**Model Compounds**

The IR spectra of compounds 1 – 4 in CH\(_2\)Cl\(_2\) are depicted in Figure 3-3A. The IR spectrum of 3 shows the characteristic features of naphthalimides: four bands are observed in the C=O region. The bands at 1698 and 1660 cm\(^{-1}\) are assigned to the symmetric [\(\nu_s(CO)\)] and antisymmetric [\(\nu_as(CO)\)] C=O stretching modes respectively, while the other two bands at 1630 and 1603 cm\(^{-1}\) originate from aromatic ring vibrations [\(\nu(Ar)\)]. The B3LYP calculation predicts a similar band pattern: four bands in the spectral range of interest, at 1707 [\(\nu_s(CO)\)], 1673 [\(\nu_as(CO)\)], 1618 [\(\nu(Ar)\)] and 1565 cm\(^{-1}\) [\(\nu(Ar)\)].

**Figure 3-3** Amide I region of the IR spectra of 1 – 4 in (A): CH\(_2\)Cl\(_2\) and (B): THF. The spectra have been scaled to the intensity of the \(\nu_s(CO)\) band at ~1700 cm\(^{-1}\).

In the C=O stretching range of the IR spectrum of the model compound 4 in CH\(_2\)Cl\(_2\), a broad band at 1672 cm\(^{-1}\) with a tail on the low frequency side is observed. This band was analyzed by fitting it to a sum of Lorentzian profiles, and it was found to be composed of three contributions (Figure 3-4D). The two components at 1676 and 1669 cm\(^{-1}\) arise from unperturbed C=O stretching. The red-shifted broad band at 1657 cm\(^{-1}\) is attributed to C=O stretching in the intramolecular hydrogen-bonded seven-membered ring conformations 4a and 4b (Scheme 3-2). Assuming that hydrogen bonding does not change the absorption coefficient of the C=O stretching mode, we can estimate from the relative contributions of the three Lorentzians to the absorption band that approximately one third of 4 exists in these hydrogen-bonded conformations.
For the trans conformation of 4, the B3LYP calculations predict the vibrational bands of the $\nu$(CO) modes at 1713 and 1699 cm$^{-1}$, with similar intensities. Experimentally, a band is found at 1672 cm$^{-1}$, which can be modelled as a sum of two Lorentzian peaks at 1676 and 1669 cm$^{-1}$. The agreement between experimental and calculated frequencies is not perfect, but the calculation supports the notion that there are two modes with distinctly different frequencies. A similar conclusion was drawn from 2D-IR experiments on a related succinamide rotaxane.\textsuperscript{[29]} The presence of two distinct bands implies that the C=O transition moments are not antiparallel to each other but almost perpendicular. This is in nice agreement with the B3LYP calculation, which predicts a dihedral angle of 122°. In the case of rotaxane 1 the bifurcated sets of hydrogen bonds with the macrocycle NH groups require an antiparallel configuration of the C=O groups,\textsuperscript{[34]} and indeed, for rotaxane 1 only one $\nu$(CO)$_{am}$ band is observed (see Figure 3-6B). In the internally hydrogen-bonded gauche conformation (corresponding to 4a), one band is calculated at essentially the same wavenumber as that of the trans form (1716 cm$^{-1}$), the other one at a lower frequency (1680 cm$^{-1}$). In the experimental spectrum the latter band is found at 1657 cm$^{-1}$. A comparison of the calculated energies indicates that the hydrogen-bonded form has a lower energy for the isolated molecules (2.3 kcal mol$^{-1}$), but in CH$_2$Cl$_2$ the extended form is predicted to be more stable by 1.2 kcal mol$^{-1}$. This is in good agreement with our interpretation of the IR spectra of 4, which concludes that the extended form is the predominant species.

\textbf{Figure 3-4} Partial IR spectra of 4 in THF (A): NH region and (B): Amide I region, and CH$_2$Cl$_2$ (C): NH region and (D): Amide I region. The bands in (B) and (D) were fitted to a sum of three Lorentzian profiles (dotted lines).
In the Amide I range of the IR spectrum of 4 in THF, the bands are slightly blue-shifted with respect to the corresponding peaks in CH₂Cl₂, and narrower. The NH stretching in 4, on the other hand, reveals the opposite changes, the bands being red-shifted and broadened in THF (Figure 3-4A and B). Hydrogen bonding between THF and the NH groups of 4 is most likely to be the reason for these effects. THF is a hydrogen bond acceptor, hence only a strong direct effect on the NH stretching mode is present, and a weaker indirect effect on the C=O stretching. The smaller contribution of the low-frequency Lorentzian to the band indicates that the intramolecular hydrogen bonding leading to 4a and 4b is disrupted to a large extent.

Apart from the free NH stretching band, a broad red-shifted band belonging to NH stretching in 4a and 4b is observed in CH₂Cl₂. This band pattern is characteristic for molecules in which intramolecular hydrogen bonding between amide groups is possible.[34]

Rotaxane and Thread

The IR spectra of 2 in CHCl₃, CH₂Cl₂, ClCH₂CH₂Cl, PrCN and THF are similar (Figure 3-5). In the spectral range of interest, the IR spectrum of 2 is equal to the sum of the spectra of 3 and 4, indicating the absence of significant interactions between the naphthalimide and succinamide stations. In the chlorinated solvents, all \( v(CO) \) modes are affected by the changes in solvent polarity, showing a blue-shift of the corresponding bands with increasing dielectric constant. Only the aromatic ring vibration at 1603 cm⁻¹ remains unaffected.

The IR spectrum of 1 displays a more complicated combination of bands (Figure 3-5). An important observation is that the IR spectrum does not show any indication of the existence of co-conformer \( n-H \), the \( v(CO)_{\alpha} \) band at 1698 cm⁻¹ in THF remains completely unaffected compared to 2. This is in agreement with NMR studies on co-conformer distribution in 1 in different solvents; the predominant co-conformer (>95%) is \( succ-1 \).[17] Crystal structures of succinamide-based rotaxanes show that two sets of bifurcated hydrogen bonds can exist between the macrocycle NH groups and the C=O groups of the succinamide station.[17]
In order to obtain a clearer picture of the additional bands in 1, difference absorption spectra were constructed by subtracting the scaled IR spectra of 2 from those of 1 (Figure 3-6A). As stated above, the ν(CO) modes localized on the naphthalimide station remain unaffected in 1, so corresponding bands are expected to vanish in the difference spectrum. The positive peaks in the difference spectra are contributions from the C=O stretching vibrations of the macrocycle amide groups [ν(CO)$_{mac}$. Shifts of bands of the succinamide station due to interactions with the macrocycle may give rise to negative or positive bands in the difference spectrum.

The difference spectra were fitted to a sum of Lorentzian peaks; the results are displayed in Figure 3-6B. In THF, the ν(CO)$_{mac}$ band is found at 1667 cm$^{-1}$. This band gradually shifts to 1655 cm$^{-1}$ in CHCl$_3$. In THF and PrCN a weak band is observed at 1645 and 1648 cm$^{-1}$, respectively, which may be attributed to hydrogen-bonded C=O groups of the macrocycle. Hydrogen bonding between the succ-NH groups and the mac-CO groups is possible due to the flexibility of the macrocycle: the mac-CO groups can point inward to form hydrogen bonds with the succ-NH groups. Molecular modelling and crystal structures of related rotaxanes$^{[35-37]}$ show that this binding motif can exist, but it probably plays a minor role. In the chlorinated solvents this band was not found, probably because it is obscured by the strong ν(CO)$_{mac}$ and ν(CO)$_{succ}$ bands. Due to the red-shift of the ν(CO)$_{mac}$ band towards the ν(CO)$_{succ}$ band, the overlap is larger in the chlorinated solvents.

The negative band at 1680 cm$^{-1}$ (in CHCl$_3$ at 1675 cm$^{-1}$) represents the decrease of free succ-CO groups in 1 compared to 2. The positive band near 1640 cm$^{-1}$ can be assigned to stretching of the hydrogen-bonded C=O groups in the succinamide station. The red-shift of the hydrogen-bonded relative to free ν(CO)$_{mac}$ in, for example, CH$_2$Cl$_2$ is 34 cm$^{-1}$. This is
14 cm\(^{-1}\) larger than in the case of conformers 4a and 4b relative to 4 and is caused by strong hydrogen bonding with NH groups in the macrocycle. The hydrogen bonding is stronger in 1 because two bifurcated hydrogen bonds with each succ-CO are possible, while intramolecular hydrogen bonds in 4a and 4b do not have optimal geometries. The calculated red-shifts of the \(\nu(CO)\) band in analogous hydrogen-bonded complexes of isophtalic amide and different acceptors obtained by Reckien and co-workers (35 – 40 cm\(^{-1}\)), agree well with our experimentally observed red-shift.\(^{[25]}\)

**Figure 3-6** (A): Difference IR spectra (1 minus 2) in CHCl\(_3\), CH\(_2\)Cl\(_2\), ClCH\(_2\)CH\(_2\)Cl, PrCN and THF. The spectra were obtained by subtracting the thread spectrum from the rotaxane spectrum after scaling at the \(\nu_s(CO)\)_ni band. The arrows indicate the changes in this range of solvents. (B): Fitting result of the difference absorption spectra. The solid line is the difference spectrum in THF. The spectra were fitted to a sum of three or four Lorentzians (dotted lines). The peak positions in all solvents are given as numbers.

Remarkably, the hydrogen-bonded \(\nu(CO)\)_succ band lies within 2 cm\(^{-1}\) in the chlorinated solvents (1639 – 1641 cm\(^{-1}\)), while all other bands related to the amide or imide groups in 1 and 2 are solvatochromic (see below). The absence of a solvent effect implies shielding of the C=O groups from the solvent by the macrocycle. In PrCN this band appears at 1634 cm\(^{-1}\), which is almost the same as in THF. The difference in behavior compared with the chlorinated solvents is probably caused by the hydrogen bond accepting properties of PrCN and THF. Hydrogen bonding of the solvents with the NH groups of the amides in the succinamidic moiety reduces the corresponding C=O stretching frequency.

### 3.2.2 Solvent effect

The IR frequencies of 1 and 2 undergo substantial red-shifts in the solvent range THF, PrCN, ClCH\(_2\)CH\(_2\)Cl, CH\(_2\)Cl\(_2\), and CHCl\(_3\). The shifts are not systematic with the dielectric constant of the solvent; hence evaluation of specific solvent effects such as hydrogen bonding and donor-acceptor interaction is required. The evaluation of specific and non-
specific solvent effects is often conducted using linear solvation energy relationships (LSER).\[38\] The effect of a solvent on a given vibrational mode can be described by Eq. 3-1.\[39\]

\[ \nu = \nu_0 + \sum_i \alpha_i P_i \]  

**Eq. 3-1**

In this equation, \( \nu \) is the wavenumber of the absorption band in the particular solvent, \( P_i \) is one of the solvent parameters: acceptor number\[40\] (AN), donor number (DN), polarity\[a\] (Y) and polarizability\[b\] (\( \Pi \)). The response of the observed effect to the respective solvent parameter is described by \( \alpha \) and \( \nu_0 \) is the wavenumber for the case that all \( P_i \)'s are zero.

The solvent-induced shifts of the IR frequencies of 1 and 2 were evaluated with this LSER method. The wavenumbers of the \( \nu_{(CO)} \) and \( \nu_{(Ar)} \) bands of 2 were taken directly from the IR spectra. Because of band overlap, the \( \nu_{(CO)} \) band of 2 and \( \nu_{(CO)} \) band of 1 were obtained from peak fitting (see Figure 3-6B). The strongest correlation was found with the solvent acceptor number. The results of this analysis are presented in Figure 3-7 and Table 3-1.

![Figure 3-7](image)

**Figure 3-7** Plot of wavenumbers of \( \nu_{(CO)} \), \( \nu_{(Ar)} \) and \( \nu_{(CO)} \) in 2 (— — —) and \( \nu_{(CO)} \) in 1 (— — —) versus the solvent acceptor number (AN). The obtained values of \( \nu_0 \), \( \alpha \) and correlation coefficient \( R^2 \) are listed in Table 3-1.

The solvent acceptor number is a measure of the solvent electrophilicity.\[40\] The negative value for \( \alpha \) demonstrates a red-shift of the corresponding vibrational mode, which in turn is

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[a] Derived from static dielectric constant \( \varepsilon \) as: \( Y = (\varepsilon - 1)/(\varepsilon + 2) \), see reference [39].

[b] From solvent refractive index \( n \) using: \( \Pi = (n^2-1)/(n^2+2) \), see reference [39].
Chapter 3

a result of bond weakening. So, in the more electrophilic solvents, electron density is withdrawn from the bonds associated with the vibrational mode. The absolute values of $\alpha$ reveal that the C=O stretching frequencies, in particular those of the exposed C=O groups in the macrocycle, are more sensitive to the solvent acceptor number than the C=C stretching in the aromatic ring of the naphthalimide $[\nu(\text{Ar})_{\nu}]$.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Compound</th>
<th>$\nu_0$</th>
<th>$\alpha$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu(CO)_{ni}$</td>
<td>2</td>
<td>1705.8 ± 0.5</td>
<td>-0.40 ± 0.03</td>
<td>0.983</td>
</tr>
<tr>
<td>$\nu(CO)_{succ}$</td>
<td>2</td>
<td>1682 ± 2</td>
<td>-0.33 ± 0.10</td>
<td>0.795</td>
</tr>
<tr>
<td>$\nu(CO)_{mac}$</td>
<td>1</td>
<td>1673 ± 2</td>
<td>-0.72 ± 0.12</td>
<td>0.922</td>
</tr>
<tr>
<td>$\nu(\text{Ar})_{\nu}$</td>
<td>2</td>
<td>1632.2 ± 0.3</td>
<td>-0.15 ± 0.02</td>
<td>0.964</td>
</tr>
</tbody>
</table>

3.2.3 NH stretching

The NH regions in the IR spectra of 1 and 2 are depicted in Figure 3-8. Despite the poor signal-to-noise ratio, clear bands can be distinguished. The NH stretching band of free NH groups in thread 2 in CHCl$_3$ appears at 3443 cm$^{-1}$ and shifts to 3436 cm$^{-1}$ and 3432 cm$^{-1}$ in CH$_2$Cl$_2$ and CICH$_2$CH$_2$Cl, respectively. The contribution of the hydrogen-bonded NH stretching due to conformers with an intra-succinamide hydrogen bond is present as a broad band centred around 3300 cm$^{-1}$. Although it is impossible to make a good estimate of the integrated intensity of this band, it appears that only a small fraction of the NH

![Figure 3-8](image-url) NH stretching region of IR spectra of rotaxane 1 and thread 2 in CHCl$_3$, CH$_2$Cl$_2$, CICH$_2$CH$_2$Cl, PrCN and THF. All spectra have been scaled to the intensity of the $\nu(CO)_{\nu}$ band at ~1700 cm$^{-1}$. 
groups is hydrogen bonded. In PrCN and THF the NH stretching bands are significantly broadened and red-shifted to 3385 cm⁻¹ and 3339 cm⁻¹, respectively, due to hydrogen bonds between the solvent molecules and the succinamide NH groups.

In the NH stretching region of the IR spectrum of rotaxane 1, bands can be distinguished that can be assigned to the succinamide station and the macrocycle. In the chlorinated solvents, the NH stretching band of the succinamide station is centred near 3425 cm⁻¹, which is at slightly lower frequency (shift ~10 cm⁻¹) than in thread 2. The macrocycle NH stretching appears as a broad band with a maximum at 3365 cm⁻¹. While the Amide I band shows a substantial solvent effect in the chlorinated solvents, the macrocycle NH stretching is unaffected by the solvent polarity. These NH groups are situated in the interior of the macrocycle and are shielded from the solvent. In PrCN and THF, this band is red-shifted, indicating that the solvent also forms hydrogen bonds with the macrocycle when its NH groups are not involved in hydrogen bonds with the thread.

### 3.2.4 Infrared Spectroelectrochemistry

The electrochemistry of 1 and 2 was already studied in detail. The CV response of thread 2 in THF exhibits a reversible, one-electron wave corresponding to reduction and back oxidation of the naphthalimide group (-1.41 V vs. SCE). Rotaxane 1, on the other hand, displays an irreversible behavior. This irreversibility is due to shuttling: the species formed after reduction is n-1⁺, which has a more positive oxidation potential than the bare radical anion 2⁺.

**Amide I**

Upon one-electron reduction of model compound 3, three new bands of 3⁻⁻ appear at 1616, 1565 and 1534 cm⁻¹ at the expense of the ν(CO)ₙₙ bands at 1703 and 1667 cm⁻¹ and the ν(Ar)ₙₙ band at 1631 cm⁻¹ in 3 (Figure 3-9). Calculation of the vibrational frequencies of 3⁻⁻, predicts the three bands to be stronger than for the neutral molecule, and shifted to 1633 [ν(CO)ₙₙ], 1589 [ν(CO)ₙₙ] and 1532 cm⁻¹ [ν(Ar)ₙₙ], which agrees well with the experimental result. An additional aromatic ring vibration at 1558 cm⁻¹ is predicted, but with a very low intensity. The calculation shows that the normal modes associated with the three bands are similar in the radical anion and in the neutral molecule, and also that the order of the frequencies is the same. The C=O stretching modes have a larger shift than the aromatic ring vibration, but the latter is substantial as well. Because the singly occupied molecular orbital in 3⁻⁻ is strongly delocalized over the whole π-system, not only the C=O but also the C=C bonds are weakened compared to those in 3.

A similar picture emerges for 2⁻⁻ (Figure 3-10). In this case, the characteristic band pattern of the succinamide station between 1700 and 1640 cm⁻¹, in 2 obscured by the ν(CO)ₙₙ band, is clearly visible in the radical anion. The tail on the red side of the ν(CO)ₙₙ band of 2⁻⁻ at 1616 cm⁻¹ (not present in the spectrum of 3⁻⁻), supports the existence of a
small fraction of \( 2^{\text{--}} \) in which hydrogen bonds exist between the succinamide station and naphthalimide radical anion (folded conformations, see Scheme 3-3).

In the course of the reduction of rotaxane 1, the three naphthalimide bands at 1702, 1667 and 1631 cm\(^{-1}\) gradually disappeared and new bands at 1591, 1546 and 1518 cm\(^{-1}\) grew in. The initially obscured \( \nu(CO)_{\text{mac}} \) and \( \nu(CO)_{\text{succ}} \) bands in 1 are visible in \( 1^{\text{--}} \). The \( \nu(CO)_{\text{mac}} \) band has shifted to lower wavenumber and appears at 1660 cm\(^{-1}\) (Figure 3-10).

**Figure 3-9** Amide I region of the IR spectra of the naphthalimide model compound 3 (—), \( 3^{\text{--}} \)(---) and difference spectrum (3\(^{\text{--}}\) minus 3) (- - -) in THF.

**Figure 3-10** IR spectra of neutral (—) and reduced (---) rotaxane 1 and thread 2 in THF.
The NH stretching region in the IR spectrum of the neutral molecule and radical anion of the rotaxane (1 and $1^-$) and the thread (2 and $2^-$) in THF are depicted in Figure 3-11. In the spectrum of $2^-$ an intensity decrease of the NH stretching band at $3340 \text{ cm}^{-1}$ is observed, while the red-shifted band of more strongly hydrogen-bonded NH stretching increases. This supports the presence of hydrogen bonds between the NH groups of the succinamide station and the C=O groups of the naphthalimide radical anion in the folded conformation ($folded-2^-$, see Scheme 3-3). The relative intensities of the free and hydrogen-bonded NH stretching indicate that the extended-$2^-$ conformation is the predominant species.

The NH stretching region of the reduced rotaxane $1^-$ reveals some interesting features. The NH stretching band of the less strongly bound NH groups in the macrocycle ($3365 \text{ cm}^{-1}$) has almost disappeared. The band of the NH stretching at $\sim3300 \text{ cm}^{-1}$ is more intense.
than in neutral 1. The stronger hydrogen bonding interactions in 1\(^{\bullet}\) compared to 1 support the notion that the macrocycle is indeed hydrogen-bonded to the naphthalimide radical anion.

**Difference spectra**

A convenient way to analyze the processes accompanying the reduction is by comparing the difference absorption spectra between radical anion and neutral molecule for rotaxane 1 and thread 2 (Figure 3-12). In both rotaxane and thread three negative bands are present. For 2\(^{\bullet}\), three prominent new bands appear in the IR spectrum at 1616, 1565 and 1534 cm\(^{-1}\). These bands are shifted to lower wavenumbers in 1\(^{\bullet}\) and appear at 1591, 1551 and 1518 cm\(^{-1}\). The larger shift to lower wavenumbers of the naphthalimide radical anion bands in 1\(^{\bullet}\) with respect to those of 2\(^{\bullet}\) provides clear evidence that translational movement of the macrocycle from the succinamide station to the naphthalimide radical anion has taken place in 1\(^{\bullet}\). This spectral red-shift in 1\(^{\bullet}\) is induced by hydrogen bonding between the NH groups of the macrocycle and the carbonyls of the radical anion. A red-shift in 2\(^{\bullet}\) (compared to 3\(^{\bullet}\)) appears only as a shoulder on the main band (1616 cm\(^{-1}\)), and hydrogen bonding of the imide anion with the succinamide NH groups (folded 2\(^{\bullet}\)) is of minor importance. In analogy with the situation in 2\(^{\bullet}\), the extended conformation of 1\(^{\bullet}\) is expected to be the predominant species.

![Figure 3-12](image)

**Figure 3-12** (A): Difference absorption spectra (radical anion minus neutral) of rotaxane 1 (---) and thread 2 (--) in THF. (B): Structures of the naphthalimide radical anion in the rotaxane (1\(^{\bullet}\)) and the thread (2\(^{\bullet}\)), with wavenumbers of the most important IR modes characteristic for the binding of the macrocycle to the naphthalimide radical anion.

In the difference absorption spectrum of the rotaxane two additional positive bands at 1658 and 1681 cm\(^{-1}\) are present. The first band (1681 cm\(^{-1}\)) has the same position as the \(\nu(CO)_{\text{succ}}\) band in 4, and belongs to \(\nu(CO)_{\text{nuc}}\), that has been liberated after shuttling. The
second band in the difference spectrum at 1658 cm$^{-1}$ is due to the red-shift of the macrocycle C=O stretching of $\text{n}1^{-}\text{1}^{+}$. The precise position of this band is at 1660 cm$^{-1}$ in the IR spectrum in Figure 3-10. The red-shift of 7 cm$^{-1}$ is due to an indirect effect of hydrogen bonding to the NH groups of the amides (see section 3.4). The computational study of Reckien et al. reports shifts of -5 to -16 cm$^{-1}$ for similar cases.$^{[25]}$ In the predominant co-conformer $\text{n}1^{-}\text{1}^{+}$ (Scheme 3-1), the hydrogen bonds from the macrocycle NH groups to the radical anion are stronger than those in co-conformer succ$^{-}\text{1}^{+}$, which causes further weakening of the macrocycle C=O bond and, as a consequence, a more red-shifted C=O stretching is observed. Another consequence is that also the Amide II band ($\sim$1540 cm$^{-1}$ in 1) of the macrocycle amide groups is expected to change. A shift to higher frequency is predicted by computation.$^{[25]}$ The precise changes in the Amide II band could not be resolved due to the overlap with the $\nu_{\text{as}}(\text{CO})_{\text{n}}$ and $\nu(\text{Ar})_{\text{n}}$ bands of the naphthalimide radical anion. Conversely, the apparent changes in the latter bands can also be influenced by changes in the Amide II bands. The (unexpected) shift of the $\nu(\text{Ar})_{\text{n}}$ peak from 1534 cm$^{-1}$ in the thread 2 to 1518 cm$^{-1}$ in the rotaxane 1 is therefore uncertain. The most important bands present in the IR spectra of neutral and reduced 1 and 2 are listed in Figure 3-12 and Table 3-2.

### Table 3-2 Wavenumbers of IR modes of neutral and reduced 1, 2 and 3 in THF.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Neutral (cm$^{-1}$)</th>
<th>Radical anion (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$\nu(\text{CO})_{\text{n}}$</td>
<td>1703</td>
<td>1702</td>
</tr>
<tr>
<td>$\nu(\text{CO})_{\text{mac}}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\nu(\text{CO})_{\text{succ}}$</td>
<td>1677$^{[a]}$</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_{\text{as}}(\text{CO})_{\text{n}}$</td>
<td>1667</td>
<td>1667</td>
</tr>
<tr>
<td>$\nu(\text{Ar})_{\text{n}}$</td>
<td>1631</td>
<td>1631</td>
</tr>
</tbody>
</table>

[a] Free C=O  
[b] Hydrogen-bonded C=O

In order to analyze the solvent effect on the switching, IR spectroelectrochemical experiments of 1 and 2 were also carried out in PrCN (Figure 3-13). For 2$^{-}$ in PrCN, the $\nu(\text{CO})_{\text{n}}$ band shows a solvatochromic red-shift (relative to THF) and appears at 1612 cm$^{-1}$. For $\text{n}1^{-}\text{1}^{+}$ in PrCN, however, the $\nu(\text{CO})_{\text{n}}$ band remains at almost the same position (1592 cm$^{-1}$) as in THF. This, again, is clear evidence that the macrocycle shields the carbonyl groups of the station to which it is hydrogen-bonded from the solvent. This was also previously concluded from the electronic absorption spectra of the radical anion in $\text{n}1^{-}\text{1}^{+}$: the absorption maximum of 2$^{-}$ shifts to the blue in more polar solvents, but in $\text{n}1^{-}\text{1}^{+}$ it does not depend on the medium polarity because the effect of the hydrogen bonds made with the macrocycle is stronger than that of solvation.$^{[16]}$
The difference absorption spectra (radical anion vs. neutral molecule) of the rotaxane in THF and PrCN suggest that a small fraction of the radical anion is not hydrogen-bonded: absorption from free radical anion is observed at 1616, 1563 and 1534 cm$^{-1}$ in THF, suggesting that a small fraction of $\text{1}^\bullet$ exists as the $\text{succ-1}^\bullet$ co-conformer. This seems to conflict with previous studies on the co-conformer distribution of $\text{1}^\bullet$.$^{[16,17]}$ However, the presence of bands attributable to the imide radical anion in a non-hydrogen bonded form does not necessarily mean that the molecules exist in the $\text{succ-1}^\bullet$ co-conformer. Cyclic voltammetry, UV-VIS spectroelectrochemistry and transient absorption spectroscopy experiments with $\text{1}$, reveal almost quantitative conversion of $\text{succ-1}^\bullet$ to $\text{ni-1}^\bullet$ (ratio $\text{ni-1}^\bullet$/$\text{succ-1}^\bullet$ >1500).$^{[16]}$ Assuming full conversion to $\text{ni-1}^\bullet$ in the present IR experiments, we can conclude that in this co-conformer not all the C=O groups of the naphthalimide anion are involved in hydrogen bonding, and also that more than one type of hydrogen bond with different geometry and strength is present. An additional indication for this is the fact that the $\nu(CO)_{\text{ni}}$ band of $\text{ni-1}^\bullet$ (1591 cm$^{-1}$) is broad, probably composed of bands from C=O stretching of differently hydrogen-bonded C=O groups.

The switching in rotaxane $\text{1}$ is driven by the fact that hydrogen bonding between macrocycle and naphthalimide radical anion is energetically favored over hydrogen bonding between macrocycle and succinamide station, i.e. the hydrogen bonds between $\text{mac-NH}$ and $\text{ni}^\bullet$-CO are stronger than those between $\text{mac-NH}$ and $\text{succ-CO}$. This is confirmed by the fact that the $\nu(CO)_{\text{mac}}$ band exhibits a red-shift of 7 cm$^{-1}$ in $\text{ni-1}^\bullet$ compared to $\text{succ-1}$. The red-shift is obviously caused by stronger hydrogen bonds in $\text{ni-1}^\bullet$ compared to $\text{succ-1}$.

From the fact that hydrogen bonds in $\text{ni-1}^\bullet$ are stronger than in $\text{succ-1}$, one would expect a larger hydrogen bond induced red-shift of the $\nu(CO)_{\text{ni}}$ band compared to the $\nu(CO)_{\text{succ}}$.
band. However, the red-shift of the ν(CO)$_{suc}$ band of 1 in THF is 47 cm$^{-1}$ (1680 → 1633 cm$^{-1}$), while the largest shift observed in the spectrum of $n$-$1^{+}$ is for the ν(CO)$_{n}$ band (25 cm$^{-1}$). The observation that the ν(CO)$_{suc}$ band in the radical anion exhibits a smaller red-shift than the ν(CO)$_{n}$ band in the neutral molecule, means that the former is less sensitive to hydrogen bonding, but the reason for this is not obvious.

In order to understand in more detail the influence of the strength of the H-bonding interactions on the equilibrium between $suc-1^{+}$ and $n$-$1^{+}$, experiments with structurally modified rotaxanes were performed; the results of these studies are presented in Chapter 4 and 5. In these new molecular shuttles, the naphthalimide station has been replaced by other aromatic imides. Due to the different size of the aromatic core, the electron density on the carbonyl groups in the radical anion will be different. An important result of the study with a naphthalene bisimide system is that despite the smaller driving force than in the naphthalene monooimide system, shuttling still occurs to a large extent (>80%).[41] This supports the idea that in 1$^{+}$, the conversion to the $n$-$1^{+}$ co-conformer is close to quantitative. Therefore the minor fraction of apparently free C=O groups in $n$-$1^{+}$, represented by the bands at 1616 and 1563 cm$^{-1}$ (in THF) must represent a fraction of species in which not all $n$- CO groups are hydrogen-bonded to the macrocycle NH groups.

3.3 Conclusion

The Amide I region in the IR spectra of 1 and 2 in solvents of different polarity (CHCl$_3$, CH$_2$Cl$_2$, CICH$_2$CH$_2$Cl, PrCN and THF) was analyzed. In the major co-conformer of 1, the macrocycle is situated at the succinamide station. Both 1 and 2 show bands due to the naphthalimide station, originating from symmetric and antisymmetric C=O stretching and aromatic ring vibrations. All these modes are solvatochromic and exhibit a red-shift with increasing solvent acceptor number. In the IR spectrum of 2, ν(CO)$_{suc}$ bands of both free and hydrogen-bonded C=O groups were observed. In rotaxane 1, a major part of the succinamide C=O groups was found to be hydrogen-bonded to the NH groups of the macrocycle. The shift with respect to the free ν(CO)$_{suc}$ in 2 is large (in THF: 47 cm$^{-1}$) because two bifurcated hydrogen bonds can be formed with each carbonyl.[17]

The IR spectroelectrochemical experiments unambiguously show that the macrocycle undergoes translational movement from the succinamide to the one-electron reduced naphthalimide station. Upon reduction of thread 2, three new bands of the radical anion appear in the spectrum, while the bands from the neutral naphthalimide disappear. In rotaxane 1, the same bands show up, but shifted to lower frequencies. This red-shift of the C=O stretching modes is a result of bond weakening caused by hydrogen bonding with the NH groups of the macrocycle. The ν(CO)$_{n}$ band also shows a shift to lower frequency (9 cm$^{-1}$ in THF) because the amide NH groups are involved in hydrogen bonds (indirect
A remarkable observation is the shielding effect of the macrocycle. The \textit{succ}-CO and \textit{ni}-CO groups encapsulated by the macrocycle are isolated from the solvent. The corresponding $\nu$(CO) bands do not show any dependence on the solvent polarity.

### 3.4 Appendix: Calculations \textit{N}-Methylacetamide

Ab initio calculations were performed to investigate the effect of hydrogen bonding on the vibrational modes of amides. For this purpose, the wavenumbers of the $\nu$(NH), $\nu$(CO) and Amide II bands in \textit{N}-methylacetamide and a hydrogen-bonded dimer were calculated using the B3LYP/6-31G(d) model chemistry.

The obtained results (Figure 3H14) show bond weakening in the hydrogen-bonded dimer compared to the isolated molecule. Hydrogen bonding causes a frequency decrease of the $\nu$(NH) and $\nu$(CO) modes of the involved NH and C=O groups. The Amide II band on the other hand shows a frequency increase. Also the C=O and NH groups which are not directly involved in hydrogen bonding are affected and red-shifts are observed for the corresponding vibrational frequencies. The Amide II also shows a clear indirect effect: a frequency increase is observed. This indirect effect is smaller that the direct effect but still substantial.

### 3.5 Experimental Details

#### Syntheses

Compounds 1 and 2 were prepared as described in previous work.\textsuperscript{[16]} The syntheses of compounds 3 and 4 are depicted in Scheme 3-4. Compound 3 was synthesized from
precursor \(5\) in 89% yield. Compound \(5\) was prepared using a literature procedure.\(^{[16]}\) Compound \(4\) was synthesized in two steps from commercially available 2,2-diphenylethylamine and succinic anhydride in 71% yield.

**Scheme 3-4** Syntheses of naphthalimide and succinamide model compounds \(3\) and \(4\).

**N**-Butyl-2,5-di-\(\text{\textit{tert}}\)-butynaphthalimide (3). A solution of \(5\) (205 mg, 0.66 mmol) and n-butyl amine (481 mg, 6.6 mmol) in ethanol (25 mL) was refluxed overnight and stirred at room temperature for 3 days. The white precipitate was filtered off, washed with ethanol and dried in air. Product \(3\) was obtained as a white powder. Yield: 215 mg (89%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.64\) (d, 2H, aromatic H), 8.12 (d, 2H, aromatic H), 4.20 (t, 2H, N-CH\(_2\)-), 1.72 (quintet, 2H, N-CH\(_2\)-CH\(_2\)-CH\(_3\)), 1.47 (m, 20H, t-Bu + CH\(_2\)-CH\(_3\)), 0.98 (t, 3H, CH\(_2\)-CH\(_3\)). Elemental analysis: calculated (%) for C\(_{24}\)H\(_{31}\)NO\(_2\): C 78.86; H 8.55; N 3.83; O, 8.75; found C 78.20, H 8.50, N 3.98, O 9.24.

**N**-(2,2-Diphenylethyl)-succinamic acid (6). A mixture of 2,2-diphenylethylamine (5.79 g, 29.3 mmol) and succinic anhydride (4.41 g, 44.0 mmol, 1.5 equiv.) in THF was stirred overnight. The solvent was evaporated under reduced pressure and the white solid obtained was triturated with water to remove excess succinic anhydride and polar by-products. After drying, \(6\) was obtained as a light brown powder. Yield: 6.78 g (78%).

\(^1\)H NMR (400 MHz, CD\(_3\)OD): \(\delta = 7.38 – 7.16\) (m, 10H, aromatic H), 4.24 (t, \(J = 8.1\) Hz, 1H, (Ph)\(_2\)-CH-C), 3.81 (d, \(J = 8.1\) Hz, 2H, C-CH\(_2\)-N), 2.47 (t, \(J = 7.0\) Hz, 2H, C-CH\(_3\)-COOH), 2.34 (t, 2H, \(J = 7.0\) Hz, 2H, HNOC-CH\(_3\)-C).

**N**-Butyl-\(N\)'-(2,2-diphenylethyl)-succinamide (4). A solution of \(6\) (168 mg, 0.566 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added to a mixture of \(N\)-(3-dimethylaminopropyl)-\(N\)'-ethylcarbodiimide hydrochloride (EDC) (297 mg, 1.55 mmol) and 1-hydroxybenzotriazole (HOBt) (123 mg, 0.913 mmol) in CH\(_2\)Cl\(_2\) (10 mL). The mixture was stirred for 10 minutes. A solution of n-butyl amine (41.4 mg, 0.566 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was added, and the reaction mixture was stirred overnight. The solvent was evaporated and the residue was
dissolved in ethyl acetate. The solution was washed subsequently with 1M HCl (3×), saturated NaHCO₃ (3×), and water (3×). The organic layer was dried over MgSO₄ and the solvent was evaporated, affording 4 as a white powder. Yield 182 mg (91%).

¹H NMR (400 MHz, CDCl₃): δ = 7.39 – 7.18 (m, 10H, aromatic H), 5.85 (broad, 2H, NH’s), 4.16 (t, 1H, (Ph)₂CH₂C), 3.88 (dd, 2H, (Ph)₂CH₂CH₂N), 3.19 (m, 2H, NCH₂CH₂), 2.40 (s, 4H, OCC₆H₄CH₂CO), 1.46 (quintet, 2H, NCH₂CH₂CH₂), 1.34 (quintet, 2H, CH₂CH₂CH₂), 0.92 (t, 3H, CH₃CH₂CH₃). Elemental analysis: calculated (%) for C₂₂H₂₈N₂O₂: C 74.97; H 8.01; N 7.95; O 9.08; found C 74.83; H 8.56; N 7.88; O 8.67.

Infrared spectra

Sample preparation. All IR spectra were measured with 2 – 4 mM solutions. The solutions were prepared in Schlenk flasks by dissolving weighed amounts of compound under dry N₂ in freshly distilled dry solvent in order to avoid the presence of water in the samples. The solvent was added with a syringe, the volume of the obtained solution was known only approximately. The sample solutions were then transferred to the IR cell with a syringe.

Infrared Spectroelectrochemistry. IR spectroelectrochemical experiments were performed in an optically transparent thin-layer electrochemical (OTTLE) cell equipped with CaF₂ optical windows and a minigrid platinum working electrode. The optical beam can pass directly through the working electrode, allowing the redox processes taking place in the thin solution layer surrounding the working electrode to be studied spectroscopically. The controlled-potential electrochemical conversions were carried out with a PA4 potentiostat (EKOM, Polná, Czech Republic). A slow scan rate of 2 mVs⁻¹ was used, in order to allow quantitative electrochemical conversion. The spectra were recorded at different points on the thin-layer voltammograms; the scanning of the potential was paused during the recording. Dry tetrabutylammonium hexafluorophosphate (Bu₄NPF₆), crystallized twice from methanol, was used as supporting electrolyte. IR spectra were recorded on Nicolet 6700 FTIR or Bruker Vertex 70 FTIR spectrometers.

Calculations

Calculations of the IR frequencies in the Amide I region of the model compounds were carried out at the B3LYP/6-31G(d) level. For the calculations of the C=O vibrations in 4, the butyl group was replaced by a methyl group, while for 3 and 3⁺, the butyl group was replaced by an ethyl group, and the tert-butyl groups by methyl groups. For the calculation of IR frequencies in a solvent medium the polarizable continuum model (PCM) was used. The computed wavenumbers were scaled by a standard scaling factor of 0.9614.
Acknowledgements

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3.6 References


Chapter 3


Chapter 3
