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High-Frequency Vibrations of the Simplest Benzyl Amide [2]Catenane

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Infrared and Raman spectroscopies along with molecular orbital calculations are used to study—for the first time—the vibrational motions of a topologically complicated chemical system, namely a [2]catenane of the benzyl amide type. Because of the intrinsic line width of the spectra, comparison of experiments and theory is only partially successful. The insight given by the simulations—which show that the C=O normal modes are delocalized while the N–H modes are localized—is, however, useful and makes us propose a simple model that explains both the larger line width of the spectra of the catenane with respect to those of the parent macrocycle and the great sensitivity of the infrared spectrum of the catenane to the environment. Examples of such sensitivity are the frequency shifts observed upon going from KBr to CsI, features not present in the case of the macrocycle.

Introduction

Through the pioneering work of Sauvage, Stoddart, and others,1 catenanes (mechanically interlocked macrocycles) are becoming seen as important potential component structures for nanotechnology. One reason for this is that for catenanes composed largely of rigid aromatic units, the combination of the restriction in the freedom of motion of components in some directions (imposed by interlocking), together with that allowed in others, is similar to the degrees of freedom allocated to moving parts in machinery in the macroscopic world. Furthermore, their mechanically interlocked architectures allow catenanes to change the relative separation (and therefore the nature and degree of interaction) between pendant functionality on each macrocycle, by this potentially allowing switching “on” and “off” of particular properties in a manner not open to the majority of topologically trivial molecules. To develop applications of these molecules, it is clearly necessary to fully understand the nature of their inter- and intra-ring interactions. Apart from their structures, their characterization in terms of fundamental and inducible properties must performe start with the study of the electronic and nuclear motions that reflect the different time-scale dynamics present in the system. Here we report the first study of the high-frequency vibrational states of a mechanically interlocked molecule, the benzyl amide [2]catenane 1 (Figure 1). To the best of our knowledge, this is the first vibrational study of any catenane.

Large (i.e., ≥100 atoms) organic systems that contain conjugated repeat units can be loosely divided in two sets. The first consists of entirely conjugated molecules—polyenes, polyythiophenes, and porphyrins, for example. In the second, one finds molecules whose conjugated moieties are separated by saturated bridges. In terms of properties, the difference between the two sets can be highly significant. Fully conjugated molecules cannot realistically be studied as the sum of their interacting fragments. Polyyenes epitomize this kind of behavior.2 In contrast, when the building blocks are divided by one or more sp3 carbon atoms, as is the case with benzyl amide catenanes, perturbation theory can still hold and the molecular properties may be determined by analytical models in both the simplest cases of a “dimer” and even in the most complex case of an infinite chain. Difficulties—and implicitly a degree of interest—arise when the number and the roles of the interacting fragments vary.

The prototypical benzyl amide [2]catenane 1 is the simplest member of a large family of molecules prepared through a self-assembly process serendipitously discovered at UMIST.3 The system consists of four isophthalic diamide and four p-xylyl groups in the form of two identical macrocycles that are

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Figure 1. Benzyl amide [2]catenane 1: (a) solid-state structure determined by X-ray crystallography and (b) ideal structure.
mechanically interlocked and can be viewed as the sum of two sets of four isolated conjugated units. To add further similarity, every moiety is basically a derivatized phenyl group. Owing to the interlocked structure, the interactions between various individual units cannot be assumed to be the same. For example, the interaction of a fragment with a similar fragment in the same macrocycle differs from the interaction between fragments that are not located in the same macrocycles; the first is determined by a combination of through-space and through-bond interactions while the second is only through-space, although it can have an additional contribution brought about by hydrogen bonding. Furthermore, the environments and conformations of each group are not the same, at least in the solid state. Mechanical and electronic interactions can occur and modify the properties of the catenane with respect to those of the macrocyclic monomers. Vibrational spectroscopy is particularly well-suited to provide information regarding mechanical interactions. The vibrational frequencies, and their intensities or cross sections, are a function of the normal modes which, in turn, image the nuclei dynamics. Two main scenarios—and their combinations—can conceivably emerge from the spectra and their analysis: in the first, interaction between the fragments spreads the vibrational frequencies of a group over a certain range, and in the second, the different environments experienced by each spectroscopically active group sets them apart from one another. In the first instance, spectroscopy becomes a probe of the interaction between the moieties, in the second, it becomes a probe of the local environment of the groups.

The work carried out in this paper presents the results of a combination of experimental and computational, or modeling, techniques aimed at obtaining a picture of the interactions and the high-frequency vibrational dynamics of the simplest octa-benzamid [2] catenane, 1. The infrared and Raman spectra are recorded at standard resolution and compared with the result of molecular orbital calculations. The emerging picture of a strong and easily modified interplay between local vibrational oscillators is supported by a simple model and the significant differences that appear in the infrared spectra of the catenane in two different matrices.

**Experimental Procedure**

**Preparation.** [2] (1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetraazacyclohexacosan-1,7,14,20-tetraaza-2,6,15,19′-tetraoxo-3,5′,9′,12′,16′,18′,22′,25′-tetraazacyclohexacosane) Catenane (1). To a stirred solution of triethylamine (1.19 g, 18.9 mmol) in anhydrous (stabilized with amylene, not ethanol) chloroform (130 mL) under argon were added isophthaloyl dichloride (0.87 g, 4.3 mmol) in anhydrous chloroform (130 mL) and p-xylene diamine (0.57 g, 4.3 mmol) in anhydrous chloroform (130 mL) simultaneously, over 30 min using motor-driven syringe pumps. The mixture was allowed to stir overnight and then filtered. The filtrate was washed with 1 M aqueous hydrochloric acid (3 × 200 mL), then 5% aqueous sodium hydroxide (3 × 200 mL), and finally water (3 × 200 mL). The organic layer was then dried over anhydrous magnesium sulfate and concentrated under reduced pressure to afford 0.22 g (20.1%) of catenane (1); mp 315 °C (decomposes); 1H NMR (300 MHz, [D₆]DMSO) δ 8.62 (8H, s), 8.05 (4H, d), 7.88 (8H, dd), 7.50 (4H, t), 6.75 (16H, bs), 4.01 (16H, bs); 13C NMR (75 MHz, DMSO-d₆) δ 198.9, 141.3, 138.4, 133.7, 132.4, 130.8, 130.0, 46.9; FAB-MS (mNBA matrix); m/z 1065 (M + H)⁺, 533 (M/2 + H)⁺.

**Infrared Spectroscopy.** The standard resolution infrared spectra were recorded with a Fourier Transform spectrometer Bruker 113V working under vacuum (10⁻¹ Torr). The interferometer was of the Genzel type, and the resolution was set to 1 cm⁻¹. A standard DTGS detector equipped with KBr and polyethylene windows was used. The catenane or the parent macrocycle powder was mixed with 200 mg of CsI or KBr and pressed into a pellet. The infrared spectra for the comparison between the KBr and the CsI matrices were collected with a Fourier transform spectrometer BIO-RAD FT 60A equipped with a KBr beam splitter and a DTGS detector. The interferometer was of Michelson type, and the resolution was set to 2 cm⁻¹. The samples were again pellets of CsI or KBr with a 1.25% concentration in weight of the catenane or the parent macrocycle.

**Raman Spectroscopy.** The Raman spectrometer used in this study was a Bruker RFS 100 equipped with a Nd:YAG laser working at 1064 nm operated at a power of 260 mW. The resolution was set to 2 cm⁻¹. A Ge diode operating at liquid nitrogen temperature was used as a detector. The Raman measurements were performed in the backscattering configuration. The catenane powder was pressed into a small hole in a metallic pellet.

**Theoretical Background**

The semiempirical calculations carried out for this work were performed with the Gaussian 92 suite of programs. This package includes both semiempirical and ab initio procedures. In the semiempirical part, the Hessian matrix—i.e., the matrix of the second derivatives of the energy with respect to nuclear displacements—is obtained by numerical differentiation of the energy gradients. Calculation of this matrix is the rate-determining step for vibrational frequencies and normal modes. Subsequent projection of the normal modes onto the vector of the dipole moment derivatives gives the infrared intensities. This part of the program does not calculate the Raman cross sections. They can be calculated ab initio at the Hartree–Fock level, but not at the semiempirical level. The numerical differentiation used to calculate the Hessian matrix, however, can be utilized Advantageously to minimize the effort required when one extends the computer code to the Raman activities. The vector of the Cartesian derivatives with respect to the nuclear displacements can be readily obtained if at each step one adds the evaluation of the polarizability. Subsequent projection of the normal modes onto this vector furnishes the Raman activities. More in detail, the Raman cross section is proportional to ∂α²/∂Q², where α is the polarizability tensor and Q is the set of the vibrational normal modes. The procedure to calculate α² is general and can be applied both to semiempirical and ab initio wave functions. One can start from the classic expression for the energy perturbation due to an external monochromatic field, F = F₀(eᵣeᵣ + e⁻⁾ + 1)

\[ E(F) = E - μ_a F^a - \frac{1}{2} \alpha_{ab} F^b F^c - \frac{1}{3!} β_{abc} F^a F^b F^c - \cdots \] (1)

where the sum over repeated indices is implied. In eq 1, μ_a, α_{ab}, and β_{abc} stand for dipole moment, polarizability, and hyperpolarizability. The term H' = μ_a F^a is the perturbation responsible for the polarizability, in which

\[ μ = - \sum e r_j \] (2)

where the sum runs over all the electrons. Quantum chemically, the energy variation caused by the electric field can be written as
\[ \alpha_{ab} = -Tr(H^b(D^b(F))) \]  
(3)

where \( H^a \) is the dipole moment matrix in the atomic orbital basis \( \{ \chi \} \) whose matrix elements read

\[ H^b_{ab} = -\langle \chi_a | e \sigma | \chi_b \rangle \]  
(4)

and \( D^b(F) \) is the density matrix perturbed along the \( b \) direction

\[ D^b(F) = C^0(F) n C^*(0) + C(0) n C^b(0) \]  
(5)

where \( C \) is the matrix of the molecular orbitals, \( C(0) \) and \( C(F) \) are the orbitals before and after the field is switched on, and \( n \) is the occupation matrix. The perturbed molecular orbitals are calculated as

\[ C^b(F) = C^0(0) U^b(F) \]  
(6)

where the matrix elements of \( U \) are expressed in terms of the auxiliary matrix \( G \) as

\[ U^b_{ij}(F) = \frac{G^b_{ij}(F)}{\epsilon_j^0 - \epsilon_i^0} \]  
(7)

where \( i \) and \( j \) refer to occupied and unoccupied orbitals and \( \epsilon_j^0 \) is the unperturbed energy of the orbital. The auxiliary matrix \( G \) represents the perturbation in the molecular orbital basis. This scheme can converge to the final result of eq 3 via an iterative procedure:

first, the dipole moment matrix in the atomic orbital basis is built;

second, the matrix is rotated in the molecular orbital basis to give \( G \), and subsequently \( U \), \( C \), and \( D \);

third, the new perturbation is calculated with the orbitals obtained by diagonalization of the perturbed Hartree–Fock matrix, \( F^b(F) = H^b + D^b(F)[2F - K^0] \), where \( J \) and \( K \) are the Coulomb and exchange matrices;

fourth, the convergence is checked, and if not achieved steps 2 and 3 are repeated.

A detailed analysis of frequency-dependent and static properties calculated with this model up to third order has been given before.\(^5\) After numerical differentiation of the polarizability with respect to the Cartesian coordinates, the vector is projected along the normal modes. The Raman intensities, \( I_R(\text{obs}.) \), for the total light scattered in a direction perpendicular to that of the electric vector of the incident beam are obtained as

\[ I_R(\text{obs}.) = \text{const}(45\alpha^2 + 7\beta^2) \]  
(8)

where the constant is proportional to the fourth power of the field and

\[ \alpha = \frac{1}{3} (\alpha_{11} + \alpha_{22} + \alpha_{33}) \]  
(9)

and

\[ 2\beta^2 = \sum_{ij} \alpha_{ij} - \alpha_{ji}^2 + \sum_{ij} (\alpha_{ij} + \alpha_{ji})^2 \]  
(10)

The theory of the Raman scattering in terms of the polarizability tensor can be found in Califano.\(^6\) Calculations of the Raman cross sections along the scheme given above have been successful in the simulation of the spectra of \( C_{60} \), \( C_{70} \) and two isomers of \( C_{78} \).

Results and Discussion

In this work, we present the first characterization of the high-frequency vibrational motions of the parent benzylic amide [2]catenane. The intent is to obtain information on the interaction that exists in the molecule and that can be probed by infrared and Raman spectroscopy. To this end, we proceed in three steps: first, we present the spectra in rather general terms and compare them with molecular orbital calculations of the frequencies and intensities. Then we set up a very simple model that naturally yields a possible origin of line-broadening—one of the causes of the difficulties in the comparison of theory and experiments. Finally, the consequences of the model are discussed in terms of the different behavior shown by the catenane and its parent macrocycle in different salt matrices.

Introducing the Spectra. Cursory inspection of the spectra in the high-frequency region gives a fair amount of general information. The most intense, identifiable bands of the infrared spectrum shown at the top of Figure 2 can be assigned\(^9\) as follows:

Figure 2. Top: Standard resolution infrared spectrum of benzylic amide [2]catenane 1. The stick spectrum represents the MNDO frequencies scaled according to eq 11 and the corresponding intensities. Bottom: Raman spectrum of benzylic amide [2]catenane 1. The stick spectrum represents the MNDO frequencies scaled according to eq 11 and the corresponding cross sections.

It is important to emphasize that the approach outlined above cannot be used in the pre-resonant and resonant regimes where the largest contribution comes from the Franck–Condon factors of the resonant state. The Raman experiments reported in this work are strictly in the off-resonant regime, and as such the procedure outlined above is deemed adequate.
(i) 3368, 3330, 3300 cm\(^{-1}\) N–H stretches,
(ii) 3058 cm\(^{-1}\) (group of peaks) aromatic C–H stretches,
(iii) 2934 cm\(^{-1}\) (group of peaks), 2886 cm\(^{-1}\) aliphatic C–H stretches,
(iv) 1665, 1637 cm\(^{-1}\) C=O stretches,
(v) 1533 cm\(^{-1}\), amide II band, C–N stretches plus N–H bendings,
(vi) 1302 cm\(^{-1}\), amide III band, C–N stretches plus N–H bendings, and
(vii) the remaining bands at 1482, 1472, 1452, 1433, 1424, 1360, 1326, 1287, 1268, 1247, 1220, 1168, 1109, 1084, 1025, 1000, 993, 904, 859, 813, 786, 779, 769, 734, 705, 692, 686, 657, 641, 634, 605, 502, and 477 cm\(^{-1}\) are variously due to C–C stretches, CCH and CCC bendings, further amide bands, and out-of-plane distortions.

The most intense bands of the Raman spectrum shown at the bottom of Figure 2 can be assigned as:
(i) 3072, 3057, 3037 cm\(^{-1}\) aromatic C–H stretches,
(ii) 2912, 2996 cm\(^{-1}\) aliphatic C–H stretches,
(iii) 1657, 1632 cm\(^{-1}\) C=O stretches,
(iv) 1613, 1603, 1586 cm\(^{-1}\) phenyl deformation, and
(v) 1471, 1432, 1420 cm\(^{-1}\) C–H\(_2\) deformation, and
(vi) the remaining bands at 1363, 1325, 1305, 1285, 1268, 1242, 1206, 1185, 1166, 1046, 1002, 972, 954, 877, 811, 787, 698, 669, and 641 cm\(^{-1}\) are variously due to C–C stretches, CCH and CCC bendings, further amide bands, and out-of-plane distortions.

The inspection given above of the spectra furnishes general information on the molecular structure. Insight into the properties and the dynamics of the molecule requires either the decomposition of the bands in the constituent transitions or an appropriate simulation based on quantum chemical methods.

**The Calculations.** The vibrational frequencies and normal modes calculations along with the simulation of the infrared intensities and Raman cross sections were performed at the MNDO level (see Table 1). Straightforward plotting of the spectra off the computer output would be highly desirable, but for a molecule of this size, it is not a realistic possibility with the presently available quantum chemical models. Standard procedures usually employed for far smaller molecules entails the scaling of the force constants through fitting of the experimental frequencies. The large line width of the spectra made unlikely the identification of a number of frequencies sufficient to guide a fitting. We therefore decided, as a first step to improve agreement between experiment and theory, to scale the vibrational frequencies. Quite often, a common scaling factor of 0.9 has been used. We soon found that this was hardly useful for benzylic amide [2]catenate. Resorting to a more elaborate scaling function gave the best agreement when the frequencies were obtained as

\[
\nu_{\text{new}} = 0.9 \nu_{\text{calc}} - 0.22 \nu_{\text{calc}}^2
\]

where \(\nu\) is the vibrational wavenumber in cm\(^{-1}\), \(A = 0.116\), \(\nu_0\) is 2100 cm\(^{-1}\), and \(\alpha = 150\) cm\(^{-2}\). The behavior of this function is such that the largest effects are observed for the C=O stretching region; they then taper off toward zero or toward frequencies too high to be fundamentals. A similar approach, although with a different function, was used elsewhere to improve the agreement between inelastic neutron scattering experiments and their semiempirical simulation. With the frequencies obtained by this scaling equation together with the calculated infrared intensities and Raman cross sections, one can plot the stick spectra shown in Figure 2 together with their experimental counterparts. The agreement can be considered satisfactory. One should be aware of the fact that eq 11 is totally empirical and is used to improve the match between calculations and experiments. The rationale behind this approach is the observation that the inaccuracy of theory is largest in the C=O stretching region and that there is a smooth convergence toward the experimental values at low and high wavenumbers. While, this scaling function may not be general it is expected, however, that it can be transferable to other derivatives of the benzylic amide. The two most notable failures of the quantum chemical simulation are (1) the small infrared intensity in the X–H region (which is likely to require the description of the anharmonicity in the dipole moment surface\(^{(2)}\)) and (2) the lack of the prominent Raman line located around 1000 cm\(^{-1}\). It should be noticed, however, that this line is likely to be the breathing mode of the phenyl rings and as such it owes its intensity to Franck–Condon contributions that are not present in the TDHF model employed by us. On the bright side, we notice that the simulations account well for the three main bands of the infrared region between 1000 and 1700 cm\(^{-1}\) and can describe the Raman X–H region and the second most intense Raman region around 1600 cm\(^{-1}\). Apart from the comparison between experiment and simulations, the calculations provide the forms of the normal modes. Their analysis showed that they are, in general, quite delocalized over the entire molecule. An exception was found for the N–H stretches, which are strongly localized.

**The Broadening of the Bands.** To obtain a better insight in the spectra, one should consider the sources of line broadening. In a system as large as the present one—made up by 136 atoms—the information conveyed by the spectroscopic measurements is blurred by the sheer size of it. In principle, because of the low symmetry of the molecular point group, all of the 402 fundamentals can contribute to the response. The low symmetry is intrinsic to the system that is stabilized by the hydrogen bonds and the \(\pi\)-electron stacking interactions that have their most evident manifestation in the presence of only one carbonyl group pointing toward the center of each macrocycle. Intrinsically, the different environments experienced by each local oscillator can make their frequencies vary from the pristine value. For instance, the stretching frequencies of the eight COs will depend on whether they form a single hydrogen bond, a bifurcated hydrogen bond, or no hydrogen bond. Importantly, the interaction with the environment make the groups different and can localize the vibrational modes.

Even before the interaction with the environment, a simple mechanism can be shown to affect the frequencies of the different types of active groups. To introduce it, one can start by looking at the two components of the system, i.e., the individual macrocycles, and study one of them in a high-symmetry regime. For sake of simplicity, we consider the four C=O stretches—a similar argument with different parameters would hold for the other vibrational chromophores—and assume that to zeroth order they are equivalent (high-symmetry hypothesis). Because of the presence of the \(p\)-xylyl and isophthaloyl groups, two interactions are present between the groups; we call them \(\alpha\) and \(\beta\). To maintain the model qualitative, we do not assign them. In the macrocycle, every C=O stretch has one \(\alpha\) and one \(\beta\) interaction. One can write the Hamiltonian matrix associated to this problem, which reads

\[
H = \begin{pmatrix}
D & \alpha & 0 & \beta \\
\alpha & D & \beta & 0 \\
0 & \beta & D & \alpha \\
\beta & 0 & \alpha & D
\end{pmatrix}
\]
TABLE 1: Summary of the MNDO Calculations: Unscaled Vibrational Wavenumbers, $\nu$, Infrared Intensities, $i_r$, and Raman Cross Sections, $R$

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$i_r$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5786</td>
<td>1695</td>
<td>1695</td>
</tr>
</tbody>
</table>

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relevant constant of the unperturbed C–O stretch, which is proportional to the square of the wavenumber, and $\alpha$ and $\beta$ are the mass-weighed interaction force constants. With this simple prescription, the eigenvalues can be calculated even analytically. If one takes $\tilde{\nu}$ = 1650 cm$^{-1}$, $R$ = D/100, and $\tilde{\alpha}$ = D/200, the resulting four wavenumbers are 1638, 1646, 1654, and 1662 cm$^{-1}$. The associated eigenvectors show that the two central modes are infrared active. The interaction between the four C–O stretches lifts the degeneracy and leads to an increased line width. The introduction of a second noninteracting macrocycle brings about a doubling of each level. A measure of asymmetry is introduced by threading one macrocycle into the cavity of the other. The effect can be mimicked, for instance, by reducing one of the diagonal elements of the eight by eight matrix by 1 or 2% (this agrees with the fact that in the solid only one C–O points inside the ring). We emphasize, however, that this is just a possibility presented here to obtain a qualitative insight into the vibrational dynamics of the system.

Diagonalization yields the results reported in Table 2 where the infrared intensities are calculated assuming that each local oscillator has intensity one and that its contribution to the normal mode intensity is given by the square of its component in the eigenvector. Inspection of the table shows that introduction of the asymmetry redistributes the intensity and spreads even more the active frequencies. Sidebands are predicted to arise at low and high frequencies. In practice, the result is a larger line width for the C–O stretch region. Interestingly, the model also predicts a larger line width for the catenane than for the parent macrocycle.

While the picture presented above is intended to be qualitative, it can be helpful in explaining the experimental observation (see below) that the infrared spectrum of the catenane is quite sensitive to the environment. In the model, the effect of small environmental variations can be simulated by a change of the scaling factor of the diagonal element which, in turn, results in a shift of the center of the spectroscopically active band.

Figure 3 presents two selected regions of the spectra of the catenane and the parent macrocycle in KBr and CsI. We limit the comparison to the amide band II and C–O stretching regions and the N–H stretching region. Remarkably, in the case of the catenane, upon going from KBr to CsI, the amide II and C–O stretching bands are upshifted by 7–8 cm$^{-1}$, while the NH stretching band is upshifted by 30 cm$^{-1}$. These frequency shifts are very nearly absent (~1 cm$^{-1}$) in the spectra of the parent macrocycle. In agreement with the model, the line width of the spectrum of the catenane is larger than that of the
macrocycle. In the future, we plan to measure the same frequency shifts in a series of salt matrixes for at least two benzylic amide catenanes. These measurements should lead to the development of a quantitative model to understand the phenomenon.

Conclusion

In this work, we have commenced the characterization of the vibrational properties of the simplest member of the family of benzylic amide [2]catenanes. As one might have predicted, in the latter environment, the peaks associated to amide modification of the infrared spectrum of the catenane in KBr to the environment. We have found proof of this in the via bonds or via space while the NH stretching peak is downshifted by 30 cm⁻¹ of the molecule spectra is not easily accomplished. However, the very nature present one, general retrieval of information from the vibrational properties of the simplest member of the family of benzylic amide [2]catenanes. As one might have predicted, in these measurements should lead to a vibrationally based sensors.

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