Chirality Effects on the IRMPD Spectra of Basket Resorcinarene/Nucleoside Complexes


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Abstract: The IRMPD spectra of the ESI-formed proton-bound complexes of the \( R,R,R,R \)- and \( S,S,S,S \)-enantiomers of a bis(diamido)-bridged basket resorcin[4]arene (\( R \) and \( S \)) with cytosine (1), cytidine (2), and cytarabine (3) were measured in the region 2800–3600 \( \text{cm}^{-1} \). Comparison of the IRMPD spectra with the corresponding ONIOM (B3LYP/6-31(d):UFF)-calculated absorption frequencies allowed the assessment of the vibrational modes that are responsible for the observed spectroscopic features. All of the complexes investigated, apart from \([R\text{-H}3]^+\), showed similar IRMPD spectra, which points to similar structural and conformational landscapes. Their IRMPD spectra agree with the formation of several isomeric structures in the ESI source, wherein the N(3)-protonated guest establishes noncovalent interactions with the host amidocarbonyl groups that are either oriented inside the host cavity or outside it between one of the bridged side-chains and the upper aromatic nucleus. The IRMPD spectrum of the \([R\text{-H}3]^+\) complex was clearly different from the others. This difference is attributed to the effect of intramolecular hydrogen-bonding interactions between the C(2′)–OH group and the aglycone oxygen atom of the nucleosidic guest upon repulsive interactions between the same oxygen atom and the aromatic rings of the host.

Keywords: chirality · IRMPD spectroscopy · noncovalent interactions · nucleosides · resorcinarenes

Introduction

Enantioselectivity implies that the reaction of a chiral receptor with a chiral molecule preferentially yields one product enantiomer over the other. The nature of the enantioselectivity is one of the most fundamental and provocative problems in stereochemistry and its solution can only be attempted after disentangling all of the factors involved, including: 1) the interference of the reaction environment in the receptor/molecule encounters and their evolution into the products; 2) the specific configuration-dependent interactions in the unsolvated or partially solvated receptor/molecule complex; and 3) the orientation of the functionalities in the receptor/molecule adducts that affect their reaction efficiency.[1,2]

In recent years, mass spectrometry has been a powerful means for investigating the stability and reactivity of chiral complexes in the gas phase, that is, in the absence of solvation and ion-pairing phenomena.[3–24] Positive information on the structure and the conformation of covalently bonded diastereomeric ions[25] and their metal adducts[26,27] has been obtained after the recent introduction of a very powerful and sensitive technique, namely the variable-wavelength infrared multiple photon dissociation (IRMPD) spectroscopy.[28–36] In contrast, the IRMPD-based stereochemical investigation of noncovalent chiral-ion/chiral-molecule complexes has drawn much less attention.[37,38] The major difficulty in these studies arises from the fact that their diastereomeric complexes are all held together by the same strong electrostatic interactions (e.g., proton and hydrogen-bonding) and any difference in their structure and stability is the result of much-weaker factors, such as dispersion or repulsion interactions, charge transfer, and conformational effects. The consequence is that noncovalent ion/molecule diastereomers often exhibit the same IRMPD spectroscopic features, sometimes with small differences in the band intensities.[39]

Herein, we report diastereomeric proton-bound receptor/molecule complexes that show IRMPD spectra with clearly different signatures. These findings reveal an unprecedented effect of chirality on strong electrostatic interactions in gaseous ionic complexes.

As a chiral receptor, we chose the \( R,R,R,R \)- and the \( S,S,S,S \)-enantiomers of the bis(diamido)-bridged basket resorcin[4]arenes (Figure 1; henceforth denoted as \( R \) and \( S \), re-

![Figure 1. Structures of the flattened-cone bis(diamido)-bridged basket resorcin[4]arenes \( R \) and \( S \) and of cytosine (1), cytidine (2), and cytarabine (3). Inset: structure of the \( R \) enantiomer in its most-stable “open-winged” conformation.][40]
spectively) in the flattened cone conformation. Cytidine (2) and its epimer cytarabine (3) were used as chiral guests because of their ability to establish stable proton bonds with the amidocarbonyl groups on the basket resorcin[4]arenes.\cite{40–41} For comparison, the study was also extended to cytosine (1), which was used as a simplified achiral model of compounds 2 and 3. For the sake of clarity, the functional groups that belong to the host will be given in italic.

As shown in the inset of Figure 1, the most-stable “open-winged” structure of the flattened-cone R and S hosts\cite{39} displays a slight distortion of the resorcin[4]arene nucleus, presumably owing to the stereogenic centers (Figure 1, black dots) and to the resulting asymmetric orientation of the bridged side-chains (the wings) that hold two face-to-face phenyl rings. Each wing is connected to the rest of the host frame through two adjacent NH–CO moieties whose carbonyl groups point either inside, or outside the host cavity (Figure 1). The amidocarbonyl groups are connected to the adjacent NH group that was oriented in the same direction. An intramolecular hydrogen bond (henceforth denoted as NH–OC) is formed within each wing, between the CO and NH groups that are oriented inside the host cavity. The distance between the NH and CO groups that are oriented away from the host cavity is so large that a similar interaction is prevented.

**Results**

**IRMPD spectra:** The vibrational spectra of the ESI-formed proton-bound complexes were obtained by using IRMPD spectroscopy. This technique is based on a multistep absorption process followed by the fast intramolecular redistribution of the excess vibrational energy (IVR). If the IR photons are in resonance with an IR-active vibrational mode of the complex, energy can be transferred and, after several absorption steps, the ions undergo fragmentation by the functional and the 6-311+(d,p) basis set, as implemented in the Gaussian 03 set of program suites.\cite{43,44} At this level of theory, the most basic n-centers of the nucleosides were calculated by using the Lee–Young–Parr (B3LYP)\cite{43,44} correlation functional and the 6-311+ + G(d,p) basis set, as implemented in the Gaussian 03 set of program suites.\cite{45} This work is part of a project aimed at the determination of equilibrium geometry and harmonic vibrational frequencies, we decided to adopt a multistep strategy. First, the relative proton affinities (PAs) of the most-basic n-centers of the nucleosides were calculated using the Lee–Young–Parr (B3LYP)\cite{43,44} correlation functional and the 6-311+ + G(d,p) basis set, as implemented in the Gaussian 03 set of program suites.\cite{45} At this level of theory, the most basic centers of compounds 1, 2, and 3 are their N(3) and O(2) atoms (for the numbering of the nucleoside atoms, see Figure 1). The N(3) center of compound 1 was less basic than the O(2) by 0.2 kcal mol⁻¹, which is in good agreement with previous estimates.\cite{46,47} The PA gap between the same centers in compounds 2 and 3 appreciably depends upon their specific sugar puckering and orientation relative to glycone. Extensive computational study of this dependence indicated that the N(3) center of compound 2 is always more basic than the O(2) center by at least 0.2 kcal mol⁻¹ and that this gap increases to over 1.7 kcal mol⁻¹ for compound 3.\cite{48}

![Figure 2. IRMPD spectra of the ESI-formed [R-H-I]⁺; the irradiation time was kept constant over the whole frequency range.](image)

The second step involved the notion that Monte Carlo molecular mechanics (MCMM) docking and constant-temperature MD simulation of analogous proton-bound complexes with the basket resorcin[4]arene converged unambiguously towards several stable local minima in which the guest is either located on the lower rim of the host (henceforth denoted as “in”) or outside its cavity but always proton-bonded to the CO groups (henceforth denoted as “out”; Figure 4).\cite{49}
Assuming similar “in” and “out” arrangements for the N(3)- and O(2)-protonated nucleosides, we calculated the optimized geometry, relative stability, and the harmonic vibrational frequencies of their corresponding complexes at the ONIOM (B3LYP/6-31(d):UFF) level of theory. The optimized structures of \([\text{R}\cdot\text{H}\cdot1]^+\), \([\text{R}\cdot\text{H}\cdot2]^+\), \([\text{S}\cdot\text{H}\cdot2]^+\), \([\text{S}\cdot\text{H}\cdot3]^+\), and \([\text{R}\cdot\text{H}\cdot3]^+\) regioisomers are shown in the Supporting Information, Figures S1–S5, respectively. In all cases, thermochemical calculations indicated a distinct preference of their guests to be protonated at their N(3) centers, rather than at their O(2) centers, when interacting with the host amidocarbonyl moieties.

This conclusion is further supported by better correlation between the experimental spectra of a given complex and the calculated harmonic vibrational frequencies of its most stable N(3)-protonated structure (e.g., see the Supporting Information, Figure S6). Therefore, from now on, our discussion will be restricted to the ONIOM (B3LYP/6-31(d):UFF)-calculated structures and the harmonic frequencies of the complexes that involve the N(3)-protonated guests (see Tables 1–5 and the Supporting Information, Figures S1–S5).

**Discussion**

The experimental IRMPD spectra (Figure 2 and Figure 3) were invariably characterized by sharp signals that are accompanied by very broad features. It is a well-known feature of the IRMPD spectra of noncovalent adducts that contain NH and OH hydrogen-bond donors that their stretching vibrations can be more or less red-shifted and broadened, depending upon their relevant dissociation threshold.\(^{[34,46,47,50–56]}\) The broad resonances at 3100–3300 cm\(^{-1}\)
could be a signature of these effects. However, it was also possible that the same broad features arise from the co-existence of several different conformers of the complexes in the ESI source.

Figure 2 and Figure 3 also show that the relative intensity of the IRMPD peaks do not always reflect the relative intensity of the calculated absorption frequencies of the various structures (Tables 1–5). In a few cases, several of the calculated frequencies are even missing in the IRMPD spectra. The intensity of the experimental IRMPD signals is determined by the probability of depositing enough excess energy into the specific bond(s) that is involved in complex fragmentation. This probability does not only depend on the efficiency of the resonant photon absorption, but also on the efficiency of the IVR process, as well as on the dissociation energy barrier.[56] Thus, it is possible that the resonant absorption efficiency of the IVR process, as well as on the dissociation efficiency of the resonant photon absorption, but also on the fragmentation. This probability does not only depend on the energy into the specific bond(s) that is involved in complex formation.

The sharp resonances at 2960–3100 cm−1 in all of the spectra (Figure 2 and Figure 3) are essentially attributed to the C–H stretching modes in the host and will not be discussed any further. Concerning the spectrum of [R-H-I]+, the unresolved bands at 3100–3300 cm−1 cannot be taken as a signature of the “in” and “out” structures (Table 1) because their N(3)–H···OC (νs), N(4)–H···OC–H (νs), and symm H···N(4)–H···OC (νs) stretching vibrations all fall in the same broad range. A similar conclusion is reached with regards to the intense sharp resonance at 3479 cm−1, which is attributed to the strong N(1)–H stretching (νs) of cytosine in [R-H-I]+.[46,47]

As expected, this band is absent in the spectra in Figure 2 and Figure 3.

In contrast, the small IRMPD peak at 3460 cm−1 and the intense signal at 3425 cm−1 are exclusively assigned to the in-1 structure, because it corresponds to the coordinated N–H···OC (νs) and N–H···OC stretches (νs; see the in-1 structure in Figure 4 and the spectrum in the Supporting Information, Figure S6), respectively. A similar νs mode is clearly prevented in the out-1 and out-2 regioisomers (e.g., see the out-2 structure in Figure 4 and the spectrum in the Supporting Information, Figure S6). We concluded that a significant fraction of ESI-formed complex [R-H-I]+ had the in-1 structure, although the occurrence of other regioisomers, that is, out-1 and out-2, could not be excluded. It should be noted, in this context, that no appreciable signals are observed around 3349 or 3525 cm−1 (Figure 2), which could be assigned to the strong asymm H···N(4)–H···OC stretch (ν3; Table 1). Possible reasons for these findings have been discussed above.

The diastereomeric complexes [R-H-I]+ and [S-H-I]+ show almost-identical IRMPD spectra, except for some differences in the peak shape and intensity (Figure 3a,b). Apart from the obvious absence of the ν3 signal, the spectra of [R-H-I]+ and [S-H-I]+ are very similar to that of [R-H-I]+. Indeed, they both exhibit a pronounced signal at 3425 cm−1, which is attributed to the ν3 stretch in the corresponding in-1 structure. This assignment is supported by the fact that the in-1 [S-H-I]+ structure is the most stable (Table 2). The same could not be said for the [R-H-I]+ diastereomer, for which out-1 is the most stable structure (Table 3). The formation and detection of structures other than the most stable ones is by no means unusual in ESI-MS. It may happen that aggregates that are not stable in solution are formed in the ESI microdroplets and released in the gas phase.
Table 3. Experimental and ONIOM (B3LYP/6-31(d):UFF)-calculated vibrational frequencies for the most-stable [R-H2]* structures.

<table>
<thead>
<tr>
<th>Experiment [cm⁻¹]</th>
<th>O NIOM (B3LYP/6-31(d):UFF)-calculated frequencies [cm⁻¹][a]</th>
<th>Mode description[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in-1 (9.1)[c]</td>
<td>in-2 (12.5)[c]</td>
</tr>
<tr>
<td>3100–3300 (broad)</td>
<td>3158 (vs)</td>
<td>3253 (s)</td>
</tr>
<tr>
<td></td>
<td>3217 (vs)</td>
<td>3164 (vs)</td>
</tr>
<tr>
<td>3425</td>
<td>3400 (vs)</td>
<td>3406 (s)</td>
</tr>
<tr>
<td></td>
<td>3449 (w)</td>
<td>3438 (w)</td>
</tr>
<tr>
<td></td>
<td>3480 (vw)</td>
<td>3489 (vw)</td>
</tr>
<tr>
<td></td>
<td>3500 (vw)</td>
<td>3493 (vw)</td>
</tr>
</tbody>
</table>

[a] See footnote [a] in Table 1. [b] See mode descriptions in Table 1. [c] See footnote [c] in Table 2.

Table 4. Experimental and ONIOM (B3LYP/6-31(d):UFF)-calculated vibrational frequencies for the most-stable [S-H3]* structures.

<table>
<thead>
<tr>
<th>Experiment [cm⁻¹]</th>
<th>O NIOM (B3LYP/6-31(d):UFF)-calculated frequencies [cm⁻¹][b]</th>
<th>Mode description[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in-1 (6.3)[c]</td>
<td>in-2 (11.6)[c]</td>
</tr>
<tr>
<td>3100–3300 (broad)</td>
<td>3169 (vs)</td>
<td>3280 (s)</td>
</tr>
<tr>
<td></td>
<td>3230 (vs)</td>
<td>3136 (vs)</td>
</tr>
<tr>
<td></td>
<td>3377 (vs)</td>
<td>3392 (s)</td>
</tr>
<tr>
<td>3420 (sharp)</td>
<td>3403 (s)</td>
<td>3454 (w)</td>
</tr>
<tr>
<td></td>
<td>3482 (vw)</td>
<td>3482 (vw)</td>
</tr>
<tr>
<td></td>
<td>3502 (vw)</td>
<td>3497 (vw)</td>
</tr>
</tbody>
</table>

[a] See footnote [a] in Table 1. [b] See mode descriptions in Table 1. [c] See footnote [c] in Table 2.

phase as kinetically trapped isomers. Therefore, it is reasonable to assign the sharp 3425 cm⁻¹ signal (Figure 3a, b) to the in-1 structures of [R-H2]* and [S-H2]*, with the possible contribution from the “out” regioisomers.

The same view applies to the [S-H3]* complex, whose spectrum is qualitatively similar to those of [R-H2]* and [S-H2]* (cf. Figure 3a, b, d). In contrast, the spectrum of [R-H3]* displays a signal at 3354 cm⁻¹ that has never been observed in the spectra of its isomers (cf. Figure 3c with Figure 2 and Figure 3a, b, d). At this point, several questions arise: 1) what is the origin of this new peak, and 2) why is this signal absent in the spectra of all of the [R-H3]* isomers studied (Table 4)?

In Figure 5, the calculated N(3)H···OC and symm H···N(4)H···OC frequencies of the “out” isomers are shown as a function of their corresponding N(3)H···OC distances. As expected, the N(3)H···OC (v₁) frequencies decrease with the length of the N(3)H···OC hydrogen bond (Figure 5). This trend is opposite to that of the corresponding symm H···N(4)H···OC (v₁) frequency. This means that, in the “out” structures, the N(3)H···OC interaction is more intense, whereas the HN(4)H···OC is less intense. Moreover, Figure 5 shows that, in general, the N(3)H···OC bond was stronger in the “out” structures of [S-H3]* (red circles) and [R-H3]* (black circles) than in those of [S-H2]* (blue circles) and [R-H2]* (green circles). Compared to the corresponding complexes with R as the host, the [S-H3]* and [S-H2]* complexes exhibit large differences in their N(3)H···OC distances (≥0.1 Å). These findings may be due to repulsive forces between the aglycone oxygen atom of the host and the aromatic rings of the host (C=O–π repulsion), which depend on the orientation of the C2=O–OH bond in the sugar moiety of the guest (Figure 6).

In compound 3, the C(2')–OH bond is oriented in such a way as to allow hydrogen bonding with the aglycone oxygen atom (broken green line in Figure 6c,d) and, thus, to lower its C=O–π repulsion. No hydrogen-bonding interactions are allowed in compound 2 between the aglycone oxygen atom and the C(2')–OH bond because of the unfavorable orientation of the latter moiety. Therefore, the C=O–π repulsion is more intense and the N(3)H···OC interaction is weaker. Furthermore, Figure 6 shows the opposite disposition of the sugar moiety of the guest relative to the aromatic wings of the R and S hosts, which may account for the comparatively large difference between the strengths of the N(3)H···OC interactions in the complexes with S as the host.

The plot of Figure 5 explains why the spectra of both the [R-H2]* (Figure 3a) and [S-H2]* (Figure 3b) complexes show broad bands peaking at ca. 3190 and ca. 3250 cm⁻¹. The first can be attributed to the N(3)H···OC (v₁) stretching (e.g. the blue and green open circles in Figure 5) and the second to the symm H···N(4)H···OC (v₁) one (e.g. the blue and green full circles in Figure 5). The N(3)H···OC (v₁) stretching in the [R-H3]* and [S-H3]* structures is located beneath the C-H stretching region (2960-3100 cm⁻¹) (the black and red open circles in Figure 5). Instead, the symm H···N(4)H···OC (v₁) stretching in [S-H3]* mingles either in the unresolved 3200-3300 cm⁻¹ band (the red full circles at ca. 3250 cm⁻¹ for “out-I”) or in the 3420 cm⁻¹ peak of its in-I structure (the red full circles at 3413 cm⁻¹ for “out-2”).

The calculated symm H···N(4)H···OC (v₁) stretches of the “out-1, out-2, and out-5 regioisomers of [R-H3]* also overlapped in the unresolved 3200-3300 cm⁻¹ region (Figure 5, black circles; Table 5). However, the same stretching frequencies in the “out-3 and “out-4 isomers fall at about 3350 cm⁻¹, that is, in the spectroscopic region in which [S-H3]*, [R-H2]*, and [S-H2]* does not exhibit any signals.
These assignments confirmed that ESI of methanolic solutions of nucleoside/resorcin[4]arene mixtures generates several co-existing regioisomers of their proton-bound complexes in which the nucleosidic guest was either kinetically trapped inside or outside the host cavity. The strength of the noncovalent interactions in these complexes depends on the possibility of hydrogen-bonding interactions in the nucleoside from the C(2′)/C0OH group and the oxygen atom of the aglycone. The presence of this H-bond moderates the repulsive interactions between the aglycone oxygen atom and the aromatic rings in the host. The frequency of \( \text{symm} \frac{H}{C0}N(4)/C0H \cdots OC(n3) \) in the “out” complexes was significantly affected by the subtle interplay among the host/guest attractive and repulsive interactions. Whilst the \( n3 \) frequencies of the isomers of \([S\cdot H\cdot 3]+\), \([S\cdot H\cdot 2]+\), and \([R\cdot H\cdot 2]+\) coalesce into broad bands, those of several “out” \([R\cdot H\cdot 3]+\) structures were blue-shifted from the same region and, therefore, can be discerned.

**Conclusion**

Herein, we report the first case of diastereomeric noncovalent complexes that show clearly different IRMPD spectra.

**Table 5.** Experimental and ONIOM (B3LYP/6-31(d):UFF)-calculated vibrational frequencies for the most-stable \([R\cdot H\cdot 3]+\) structures.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>ONIOM (B3LYP/6-31(d):UFF)-calcd frequencies [cm(^{-1})]</th>
<th>Mode description(^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in-1 (8.7)(^{[a]}) in-2 (10.8)(^{[a]}) out-1 (0.4)(^{[a]}) out-2 (5.9)(^{[a]}) out-3 (6.9)(^{[a]}) out-4 (8.6)(^{[a]}) out-5 (10.9)(^{[a]})</td>
<td></td>
</tr>
<tr>
<td>3180–3300 (broad)</td>
<td>3171 (vs) 3251 (s) 3075 (vs) 3184 (vs) 3029 (vs) 3296 (w) 3134 (s)</td>
<td>( v_1 )</td>
</tr>
<tr>
<td>3354 (broad)</td>
<td>3227 (vs) 3161 (vs) 3282 (s) 3276 (vs) 3354 (s) 3349 (vs) 3255 (vs) 3273 (vs)</td>
<td>( v_2 )</td>
</tr>
<tr>
<td>3425 (sharp)</td>
<td>3405 (s) 3441 (w) 3382 (w) 3386 (w) 3391 (w) 3370 (w) 3383 (w)</td>
<td>( v_3 )</td>
</tr>
<tr>
<td>3484 (vw)</td>
<td>3487 (ww) 3494 (ww) 3488 (vw) 3486 (ww) 3496 (vw) 3479 (vw)</td>
<td>( v_3 )</td>
</tr>
<tr>
<td>3502 (vw)</td>
<td>3491 (ww) 3505 (ww) 3505 (vw) 3506 (vw) 3506 (vw)</td>
<td>( v_3 )</td>
</tr>
</tbody>
</table>

[a] See footnote [a] in Table 1. [b] See mode descriptions in Table 1. [c] See footnote [c] in Table 2.
The complexes are generated in the gas phase by electro-spray ionization (ESI) of mixtures that contain a chiral host, that is, pure enantiomers of the bis(diamido)-bridged basket resorcin[4]arene, and achiral and chiral guest molecules, such as cytosine, cytidine, and its epimer, cytarabine. The proton-bound complexes with cytosine as a guest exhibit IRMPD spectra that, in light of ONIOM (B3LYP/6-31(d)/UFF) calculations, are consistent with the occurrence of several isomeric structures, in which the N(3)-protonated guest is either accommodated inside the host cavity (the “in” structure) or outside it (the “out” structure). A similar picture was observed for the ESI-formed diastereomeric proton-bound complexes with cytidine and cytarabine as guests. However, the complex between cytarabine and the $R,R,R,R$-enantionomer of the host shows a spectroscopic pattern that is clearly different from the others. This difference is attributed to the effects of the intramolecular hydrogen bonding between the C(2)–OH group and the aglycone oxygen atom of the nucleoside guest upon repulsive interactions between the same oxygen atom and the aromatic rings of the host.

**Experimental Section**

**Chemicals:** Enantiomerically pure basket resorcin[4]arenes R and S, in their flattened-cone conformation, were synthesized and purified according to literature procedures. Compounds 1–3 were purchased from a commercial source and used without further purification.

**IRMPD spectroscopy:** All of the proton-bound complexes were generated in a modified Bruker Esquire 6000 quadrupole ion trap by electro-spray ionization (ESI) of methanolic mixtures of the basket resorcin[4]arene and the nucleoside. The IR beam was focused in the ion trap through a conical hole in the ring electrode. IR spectroscopy in the range $\nu = 2800–3600$ cm$^{-1}$ was performed by using an IR optical parametric oscillator/amplifier (OPA/OPO) system that was pumped by a 10 Hz Nd:YAG laser (650 mJ per pulse, 8 ns pulse duration). The typical output energy over this wavelength range was about 23 mJ per pulse with a spectroscopic band-width of about 5 cm$^{-1}$. 

**Computational details:** All of the calculations on the noncovalent adducts between the R and S hosts and the O- and N-protonated guests 1–3 were performed by using the hybrid quantum-mechanics/molecular-mechanics (QMMM) ONIOM method, as implemented in the Gaussian 03 package. The QM region, which included both the CO–NH–CH–CH–NH–CO sequences of the host and the entire protonated guest, was calculated by using the DFT B3LYP functional and the 6–31G(d) basis set. The rest of the host molecule constituted the MM region, for which the UFF force field was used. All of the ONIOM/B3LYP/6-31G(d) geometry-optimizations were full, without restrictions, and the stationary points were characterized as true minima by vibrational analysis. The value 0.961 was used as a scaling factor for the calculated harmonic frequencies.

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Very recently, an IRMPD study on the protonated dimers of Cin-
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