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Confinement of 1-butyl-3-methylimidazolium in cucurbiturils

Sulakshana V. Athare, Shridhar P. Gejji *

Department of Chemistry, Savitribai Phule Pune University, Pune 411007, India

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ABSTRACT

Confinement of room temperature ionic liquids (RTIL) within the macrocyclic hosts significantly alters their physicochemical properties and widens their scope of applications. In this light encapsulation of the 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF$_4$) within cucurbit[*n*]uril (CBn, n = 6–8) hosts has been analyzed employing the density functional theory. Theoretical calculations predict that the BmimBF$_4$ ion pair combines with CB6 or CB7 in 1:1 proportions whilst the complexation with CB8 complex renders 1:1 as well as 1:2 stoichiometries. The lowest energy complexes show alkyl chain of the cation penetrating within CBn cavities. Moreover the CB6 complex reveals the BF$_4$ anion is bound to methyl protons of the Bmim cation externally via hydrogen bonding. On the other hand, the CB7 and CB8 complexes facilitate interactions between BF$_4$ anion and their methine protons. The ramifications of such noncovalent binding to vibrational and NMR spectra are further deciphered using the quantum theory of atoms in molecules (QTAIM), and noncovalent interactions reduced density gradient (NCI-RDG) methods in conjunction with natural bond orbital analyses (NBO). The methyl protons of butyl chain in BmimBF$_4$ emerge with the up-field signals in ^{1}H NMR spectra as opposed to the largely deshielded methine protons which can be attributed to hydrogen bonding and enhanced aromatic character of the imidazolium ring evidenced from the nucleus independent chemical shifts.

1. Introduction

Cucurbit[*n*]urils (CBn) have attracted growing attention in the domain of supramolecular chemistry owing to diverse applications in drug delivery vehicles [1], catalysis [2] and fluorescence spectroscopy [3]. CBn hosts are obtained by condensation of glycouril and formaldehyde which exhibit varying cavity-size and shape [4]. The biocompatible CBn (n = 6–8) macrocycles possess pumpkin shaped cavities and exhibit high thermal stability [5]. These hosts are fascinating and rendered with remarkable molecular recognition ability [6] toward metal ions, ammonium or imidazolium cations [7–17].

Room-temperature ionic liquids (RTIL) based on imidazolium cations are explored as catalysts in certain organic reactions [18–20]. Their use as alternative to organic solvents however, is limited owing to large viscosities [21]. The complexation of RTILs brings about a significant variation in their physicochemical properties and hence, RTIL confined within molecular scaffolds are largely being studied experimentally [22,23]. It has been realized that the confinement of BmimBF$_4$ within CBn (n = 6–8) receptors in particular, CB8 brings about significant lowering of viscosity [24]. Besides it was inferred that mono-imidazolium ionic liquids pull CB6 into neutral water thereby enhancing its solubility [25,26]. Liu et al. showed that 1-butyl-3-methylimidazolium bromide combines in 1:1 proportions with CBn scaffolds exhibiting the distinct host-guest binding patterns which can be probed through the ^{1}H NMR experiments. The investigations on the 1-ethyl-3-methylimidazolium (Emim) bromide showed that two Emim cations are accommodated within the CB6 host. Pursuance to this Kolman et al. [27] carried out synthesis of inclusion complexes of the imidazolium based RTILs composed of cations with varying alkyl substituents from ethyl to pentyl bound to the CB6 macrocycle. Except for the Emim cation, such complexes revealed 1:1 stoichiometries wherein the alkyl group penetrates within the host whilst the imidazolium ring that excludes the cavity was held together by hydrogen bonding interactions with portals of the host. Subsequent isothermal calorimetric titration experiments by Wintgens and others on CB7 and imidazolium based RTILs suggested that the complexation is governed by van der Waals interactions arising from the alkyl chain on the cation [28]. Such noncovalent binding with its strong dependence on the number of aliphatic carbons increases steadily with the alkyl chain until it accommodated completely within the host cavity. These investigations further ascertained 1:1 stoichiometry for the complexes. It was also observed that such a complexation is accompanied by enthalpy decrease, which was maximum for the hexyl substituent.

Despite of aforementioned experimental investigations, insights on noncovalent interactions for conducing the inclusion complexes between RTILs and the CBn macrocycles derived from theory can be explored for modeling their physicochemical properties. In

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* Corresponding author.
E-mail address: spgejji@chem.unipune.ac.in (S.P. Gejji).

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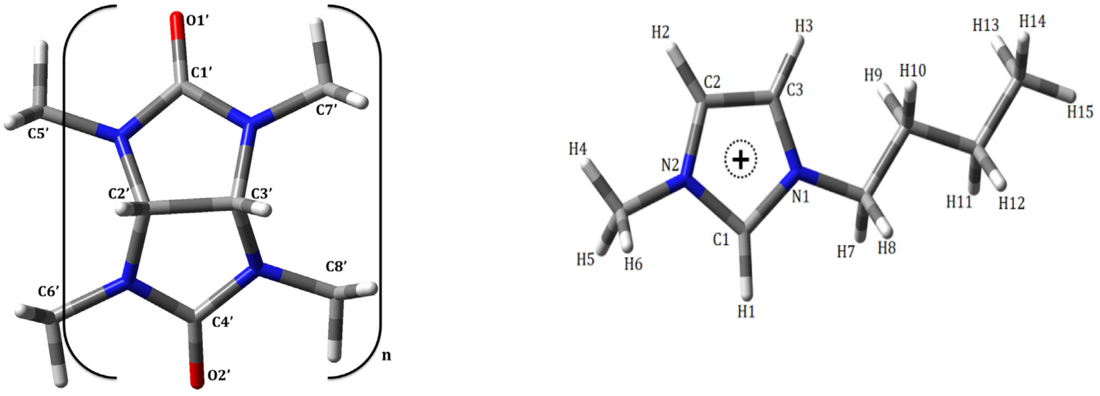
this light the present endeavor focuses on confinement of the 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) within CBn cavities and understand how hydrogen bonding, van der Waals or other dispersive interactions manifest in their structure and vibrational or ^1H NMR spectra employing the density functional theory (DFT). A systematic analysis of noncovalent interactions in hitherto inclusion complexes has thus been carried out using the natural bond orbital analyses (NBO) and quantum theory of atoms in molecules (QTAIM) incorporating the noncovalent interactions reduced density gradient (NCI-RDG) methods. The perturbations in aromatic characteristics consequent to the encapsulation of the imidazolium cation within the CBn receptors are described in terms of the nucleus independent chemical shifts (NICS).

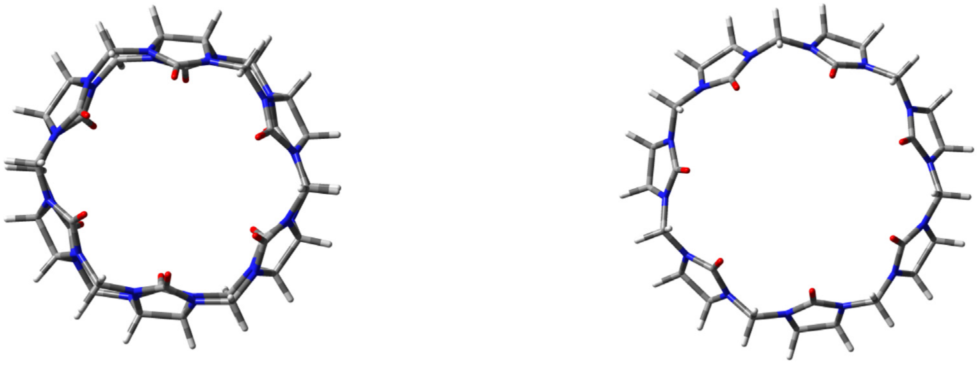
2. Computational method

Optimized structures of individual Bmim, BF_4 ions and CBn hosts were obtained using the DFT incorporating the ωB97x exchange-



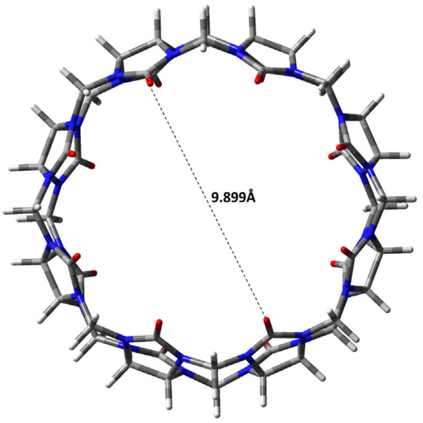
CBn monomer

Bmim cation



CB6

CB7



CB8

Fig. 1. Atomic labelling in glycouril monomer, Bmim cation and optimized structures of CBn (n = 6, 7, 8).