



Research paper

The role of London dispersion interactions in strong and moderate intermolecular hydrogen bonds in the crystal and in the gas phase

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ABSTRACT

Two variants of density functional theory computations have been applied to characterization of hydrogen bonds of the 1-(2-hydroxyethyl)-3-methylimidazolium acetate ([C₂OHmim][OAc]), i.e. with and without inclusion of dispersion interactions. A comparison of the results demonstrates that London dispersion interactions have very little impact on the energetical, geometrical, infrared spectroscopic and electron density parameters of charge-assisted intermolecular hydrogen bonds functioning both in the crystal of the [C₂OHmim][OAc] and in the isolated [C₂OHmim]⁺[OAc]⁻ ion pairs.

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1. Introduction

The possible role of dispersion interactions and their contribution to noncovalently bound complexes [1–7], van-der-Waals crystals and molecular crystals with relatively weak hydrogen bonds (HBs) [8–11] has been widely discussed. In contrast, dispersion interactions in molecular crystals with strong and moderate intermolecular HBs have been considered in only a few cases [12–15]. Herein, the results of two variants of solid-state density functional theory (DFT) computations of the [C₂OHmim][OAc] crystal (Fig. 1), i.e. with and without inclusion of dispersion interactions, were compared. Similar comparison was performed for DFT characterization of HBs in the isolated [C₂OHmim][OAc] ion pairs (Fig. 2).

2. Methods used

2.1. Evaluation of the HB energies

According to our previous experience in studies of HBs formed by charged species [16,17], two different sets of the computed properties were used in the present study for evaluation of the HB energy/enthalpy: (i) the electron density features at the HB critical point [18,19] and (ii) the spectroscopic features of the stretch-

ing vibrations of XH group (ν_{XH}) involved into HB formation [20,21].

- (i) The energy of XH...A HB (E_{HB}) can be estimated using the local electronic kinetic energy density, G_b , at the H...A bond critical point in electron density [19]:

$$E_{\text{HB}} [\text{kcal mol}^{-1}] = 269G_b [\text{atomic units}] \quad (1)$$

- (ii) Spectroscopic indicators of H-bond formation such as red shifts of ν_{XH} vibrational frequencies and increases in infrared (IR) intensities [20,21] were used to evaluate the enthalpies ($-\Delta H_{\text{HB}}$) of intermolecular HBs:

$$-\Delta H_{\text{HB}} [\text{kcal mol}^{-1}] = 0.29\Delta I^{1/2} [\text{kcal mol}^{-1}] \quad (2)$$

where $\Delta I^{1/2} = I^{1/2} - I_0^{1/2}$, and I is the IR intensity for the localized, uncoupled ν_{XH} vibration of the X-H group participating in the H-bond compared to the non-interacting group (I_0).

$$-\Delta H_{\text{HB}} [\text{kcal mol}^{-1}] = 0.33(\Delta\nu [\text{cm}^{-1}] - 40)^{1/2} \quad (3)$$

where $\Delta\nu = \nu_{\text{XH}_{\text{free}}} - \nu_{\text{XH}_{\text{bonded}}}$ represents the red-shift value of the ν_{XH} frequency caused by the formation of the HB with the XH group being the proton donor.

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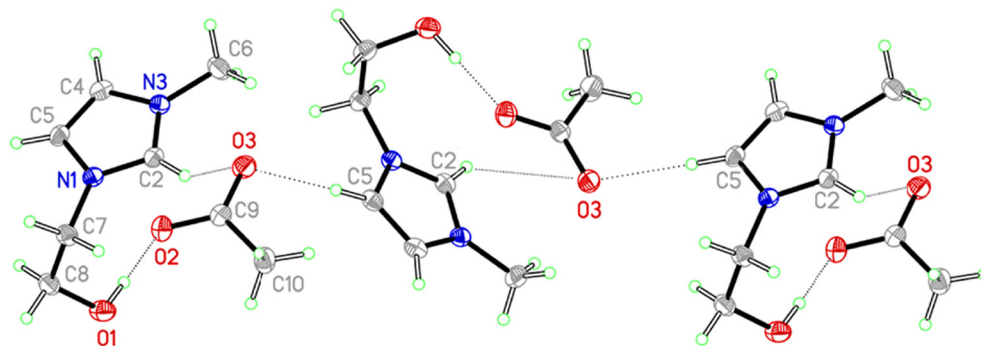


Fig. 1. ORTEP plot of the crystal structure of the 1-(2-hydroxyethyl)-3-methylimidazolium acetate ($[\text{C}_2\text{OHmim}][\text{OAc}]$) showing the main interactions between adjacent molecules by dashed lines. Created on the basis of X-ray data [16].

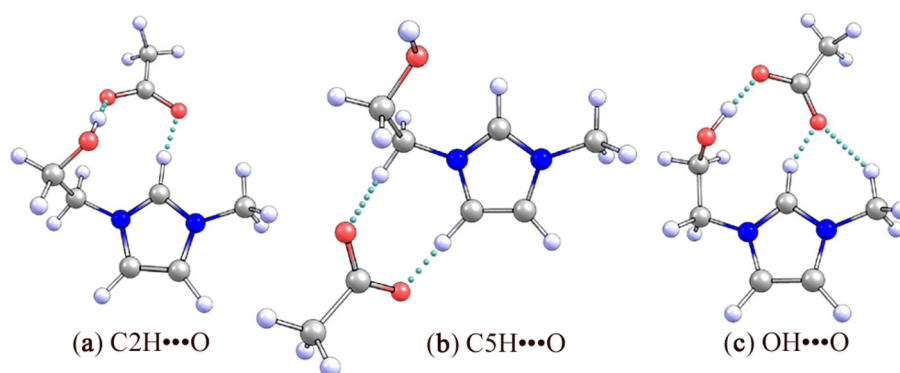


Fig. 2. Examples of optimized structures of isolated ion pairs $[\text{C}_2\text{OHmim}]^+ [\text{OAc}]^-$. HBs are indicated with dashed lines.

2.2. London dispersion interactions

In non-covalently bound systems, the correct treatment of non-local London dispersion interactions is mandatory for accurate geometries and binding energies. These interactions are not included in any semi local density functional and require dispersion corrections, for reviews and overviews see Refs. [1,2,22–24]. We used the D3 London dispersion correction in the Becke-Johnson sampling scheme (indicated by “–D3” appended to the functional name) [3,4]. The accuracy of the scheme for noncovalently bound dimers, host-guest complexes, and van-der-Waals crystals is well documented [5–7]. DFT-D3 was recently benchmarked for interactions of various ions and found to provide results close to those of CCSD(T) benchmark quality [25].

2.3. DFT computations

The calculations of the isolated ion pairs were performed with the ORCA program of version 3.0 [26]. The equilibrium structures of the ion pairs were optimized with the B3LYP hybrid functional [27,28] and the standard 6-31G** basis set. Obtained stationary points were characterized as minima by analysis of the Hessian matrices. The same combination of functional and basis set was employed for solid-state DFT computations conducted with the CRYSTAL suite of programs [29]. Further computational details can be found in [Supplementary Material](#).

The following electron density features at the $\text{H}\cdots\text{O}$ intermolecular bond critical point were considered: (i) the values of the electron density ρ_b , (ii) its Laplacian $\nabla^2\rho_b$, and (iii) the kinetic energy density G_b . The G_b values computed from the theoretical periodic

electron density were used in the present study for evaluation of HB energy (Eq. (1)).

3. Results and discussion

HB-donor and HB-acceptor units in $[\text{C}_2\text{OHmim}][\text{OAc}]$ are electrically charged, which results in strengthening of $\text{XH}\cdots\text{A}$ intermolecular HBs. Owing to this phenomenon, called charge assistance [30–35] the energy of conventional $\text{OH}\cdots[\text{OAc}]^-$ HBs and nonconventional $\text{CH}\cdots[\text{OAc}]^-$ HBs in crystals of $[\text{C}_2\text{OHmim}][\text{OAc}]$ amounts to ca. 10 and ca. 5 kcal mol^{-1} , respectively [16]. In the gas phase the energy of the both types of charge-assisted HBs increases to ca. 11–13 kcal mol^{-1} [16]. (For comparison: the energy of neutral nonconventional $\text{CH}\cdots\text{O}$ HBs in the gas phase equals to ca. 2–4 kcal mol^{-1} [36,37]). As indicated in the Introduction, little if anything is reported about the role of London dispersion forces in systems with HBs of similar strength. To quantify the contributions from dispersion interactions into the strength of the abovementioned charge-assisted HBs in the $[\text{C}_2\text{OHmim}][\text{OAc}]$ crystal, we compared in [Table 1](#) the geometrical, energetical, IR spectroscopic and electron density parameters of the strongest HBs computed with (B3LYP-D3/6-31G**) and without inclusion of dispersion interactions (B3LYP/6-31G**).

Data collected in [Table 1](#) demonstrate that the introduction of London dispersive forces in the calculation leads to a moderate lengthening of the calculated $\text{C}\cdots\text{O}$ distances by ca. 0.01 Å and a concomitant almost negligible decrease of the electron density features at the HB critical point for the $\text{CH}\cdots[\text{OAc}]^-$ HBs. Other computed structural, IR spectroscopic and electronic-topology characteristics of both conventional and nonconventional HBs do not significantly depend on the choice of the theoretical approxi-

Table 1
The values of the X...O distances $R(X...O)$ and angles $\angle X-H...O$ of the X-H...O units, where X=O or C, in the $[C_2OHmim][OAc]$ crystal from X-ray experiment and solid-state DFT computations (in parentheses). The electron density, ρ_b ; its Laplacian, $\nabla^2\rho_b$, the local electronic kinetic energy density, G_b , at the HB critical point; the HB energy, E_{HB} , and enthalpy, $-\Delta H_{HB}$; frequencies, ν , and intensities, I , of isotope-isolated XH stretching vibrations are given for each X-H...O unit.

	C2-H...O3 ^a	C5-H...O3 ^a	O1-H...O2 ^a
$R(X...O)$, Å	3.245 (3.184, 3.194) ^b	3.104 (3.085, 3.096) ^b	2.651 (2.644, 2.641) ^b
$\angle X-H...O$, deg	162 (164, 164) ^b	171 (172, 172) ^b	176 (174, 174) ^b
ρ_b , a.u.	0.021, 0.020 ^b	0.026, 0.025 ^b	0.051, 0.052 ^b
$\nabla^2\rho_b$, a.u.	0.051, 0.050 ^b	0.065, 0.063 ^b	0.140, 0.141 ^b
G_b , a.u.	0.0150, 0.0135 ^b	0.0172, 0.0172 ^b	0.0379, 0.0375 ^b
E_{HB} , kcal mol ⁻¹	4.0, 3.6 ^b	4.6, 4.6 ^b	10.2, 10.1 ^b
ν , cm ⁻¹ (I , km mol ⁻¹) for the crystal	3176 (544), 3166 (543) ^b	3183 (499), 3176 (498) ^b	3191 (1870), 3190 (1871) ^b
ν_0 , cm ⁻¹ (I_0 , km mol ⁻¹) for the isolated cation	3320 (47) 3321 (49) ^b	3303 (13), 3304 (13) ^b	3830 (74), 3833 (74) ^b
$-\Delta H_{HB}$, kcal mol ^{-1c}	4.8, 4.7 ^b	5.4, 5.4 ^b	9.6, 9.6 ^b
$-\Delta H_{HB}$, kcal mol ^{-1d}	3.4, 3.5 ^b	3.0, 3.1 ^b	8.1, 8.1 ^b

^a The original numeration of atoms taken from Fig. 1.

^b Values obtained with the use of B3LYP-D3/6-31G** computations are given in *italics*.

^c Evaluated using Eq. (2).

^d Evaluated using Eq. (3).

Table 2
The values of the X...O distances $R(X...O)$ and angles $\angle X-H...O$ of the X-H...O units, where X=O or C, in the $[C_2OHmim][OAc]$ ion pairs (see Fig. 2). The electron density, ρ_b ; its Laplacian, $\nabla^2\rho_b$, the local electronic kinetic energy density, G_b , at the HB critical point; the HB energy, E_{HB} , and enthalpy, $-\Delta H_{HB}$; frequencies, ν , and intensities, I , of isotope-isolated XH stretching vibrations are given for each X-H...O unit.

	C2H...O(a) ^a	C5H...O(b) ^a	OH...O(c) ^a
$R(X...O)$, Å	2.765, 2.756 ^b	2.803, 2.785 ^b	2.576, 2.570 ^b
$\angle X-H...O$, deg	169.7, 169.6 ^b	176.4, 172.9 ^b	175.8, 175.1 ^b
ρ_b , a.u.	0.057, 0.058 ^b	0.053, 0.055 ^b	0.065, 0.066 ^b
$\nabla^2\rho_b$, a.u.	0.036, 0.037 ^b	0.034, 0.035 ^b	0.039, 0.037 ^b
G_b , a.u.	0.040, 0.041 ^b	0.036, 0.038 ^b	0.047, 0.048 ^b
E_{HB} , kcal mol ⁻¹	10.8, 11.0 ^b	9.8, 10.3 ^b	12.8, 13.0 ^b
ν , cm ⁻¹ (I , km mol ⁻¹) for the ion pair	2534 (1844) 2549 (1800) ^b	2527 (1863) 2508 (1662) ^b	2859 (1990) 2876 (1949) ^b
ν_0 , cm ⁻¹ (I_0 , km mol ⁻¹) for the isolated cation	3320 (47) 3321 (49) ^b	3303 (13) 3304 (13) ^b	3830 (74) 3833 (74) ^b
$-\Delta H_{HB}$, kcal mol ^{-1c}	10.5 10.3 ^b	11.5 10.8 ^b	10.4 10.3 ^b
$-\Delta H_{HB}$, kcal mol ^{-1d}	9.0 8.9 ^b	9.0 9.1 ^b	10.1 10.0 ^b

^a The original numeration of atoms taken from the Fig. 1. Notation of ion pairs (in parentheses) corresponds to Fig. 2.

^b Values obtained with the use of B3LYP-D3/6-31G** computations are given in *italics*.

^c Evaluated using Eq. (2).

^d Evaluated using Eq. (3).

mation. Thus, the impact of dispersion forces on H-bonding in crystalline $[C_2OHmim][OAc]$ is moderate.

The situation is similar for the gas phase ion pairs, see Table 2, where the introduction of London dispersive forces in the calculation leads to a moderate shortening of the C...O distances by ca. 0.01–0.02 Å for the CH...[OAc]⁻ HBs and the O...O distances by ca. 0.01 Å for the OH...[OAc]⁻ HBs. These changes result in a minor variation of electron density topological parameters, ρ_b and $\nabla^2\rho_b$, of the IR intensities of the ν_{XH} bands and their vibrational frequencies. Consequently, estimates of the H-bonding strength, obtained with the use of the IR spectroscopic markers and Eqs. (2) and (3), as well as corresponding values obtained from Eq. (1), are close to each other and remain practically the same irrespective of the use of D3 correction or the neglect of dispersive forces in the computations.

Obtained results are in general agreement with the available literature data. The dispersion correction has a little influence on the atom–atom radial distribution functions and the infrared spectra of liquid water [38]. On the other hand, the dispersion interaction is

found to significantly affect some properties such as the density and the heat of vaporization [38]. According to [39], the dispersion-corrected DFT approach is needed for the accurate description of bulk water/ice equilibrium. We conclude that the applicability of the advanced computational methods with London dispersion corrections [40] for theoretical evaluation of the lattice energy of the two-component pharmaceutical crystals [41] and drug-receptor interactions [42] requires a special investigation.

It should be noted that computational predictions of IR vibrational intensities and frequencies are basis-set dependent, and B3LYP/6-31+G* level of approximation is shown to offer excellent quantitative performance in the calculations of relative 'gas-phase' IR intensities for the bands of vibrations [43], while the use of smaller basis set may lead to unreliable intensity predictions. In order to check whether the results collected in Table 2 could be influenced by the choice of basis set, the computations of the IR intensities and frequencies have been repeated at the B3LYP-D3/6-31+G* and B3LYP/6-31+G* levels of approximation. A comparison of the latter two computations (supplementary material) demonstrates quite moderate influence of D3 correction on IR spectroscopic manifestations of H-bonding, similar to the case of use of 6-31G** basis set (Table 2). Earlier we have shown that dispersion interaction has little influence on relative IR intensities computed with the hybrid DFT methods for the bands of vibrations with frequencies (ν) ≤ 2300 cm⁻¹ [44]. Present results suggest that this conclusion can be extended to the case of $\nu > 2300$ cm⁻¹.

4. Conclusions

In this letter we have shown that London dispersion interactions have little influence on the energetical, geometrical, IR spectroscopic and electron density parameters of medium to strong intermolecular HBs functioning both in the crystal of the 1-(2-hydroxyethyl)-3-methylimidazolium acetate ($[C_2OHmim][OAc]$) and in the isolated $[C_2OHmim]^+[OAc]^-$ ion pairs. In theoretical terms these results suggest that the role of dispersive forces in charge-assisted HB and in IR spectra formation is minor. In a more narrow and practical way the message is that simplified quantum chemical approaches unable to the correct treatment of nonlocal London dispersion interactions still can be applied to simulations of IR spectra. It should be noted though that the space groups and unit cell parameters of the $[C_2OHmim][OAc]$ crystal were adopted in present solid-state DFT computations, and these constraints of crystal geometry might influence the results.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2017.01.070>.

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