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Theoretical investigation on the improper hydrogen bond in κ -carrabiose \cdots Y (Y = HF, HCl, HBr, NH₃, H₂O, and H₂S) complexes

Fodil Rachida^{1,2} · Sayede Adlane³ · Sekkal-Rahal Majda¹

Abstract

The nature of H-bonds in κ -carrabiose \cdots Y (Y = HF, HCl, HBr, NH₃, H₂O, and H₂S) complexes was studied. For this aim, the structure of isolated κ -carrabiose was optimized using three global hybrids functional: B3LYP, PBE0, and M06-2X

combined with 6-311G** basis set. Subsequently, the κ -carrabiose in the presence of HF, HCl, HBr, NH₃, H₂O, and H₂S was optimized using the CBS-4 M method. NBO analyses were then carried out at the MP2/6-311G** level of theory. A particular interest was focused on C₍₁₈₎—H₍₃₄₎ \cdots Y bond. The results reveal that the C₍₁₈₎—H₍₃₄₎ \cdots Y bond is an improper H-bond since a significant contraction of C₍₁₈₎—H₍₃₄₎ was observed during the complexation leading to a significant blueshifted stretching frequency. The NBO analyses have shown that the formation of the improper H-bonds C₍₁₈₎—H₍₃₄₎ \cdots Y (Y = F, Cl, Br, N, O, and S) is principally due to the increase of the s-character of the hybrid orbital in carbon atom (rehybridization) in κ -carrabiose \cdots Y complexes. Regarding the polarization, it was proved that more the H-bond center (carbon in C₍₁₈₎—H₍₃₄₎ \cdots Y) becomes less positive, the hydrogen more positive, and Y more negative; more the contraction of the C₍₁₈₎—H₍₃₄₎ bond is important. It was also confirmed for intramolecular H-bonds in κ -carrabiose \cdots Y complexes that the rehybridization is responsible for H-bonds nature either proper or improper.

Keywords DFT · Hydrogen bonding · κ -Carrabiose · Complexes · Proper and improper hydrogen bonds

Introduction

Despite the weak interactions involved in H-bonds, the role that they play from the structural point of view is very important for many chemical and biological processes. Their formation implies a proton donating X, hydrogen (H), and a proton-acceptor Y [1–5]. The formation of the X—H \cdots Y bond is due to the interaction between the electropositive hydrogen atom and an electronegative atom that can be a heteroatom (O, N, S, P, or halogen) or a region with a high electronic density as electron π cloud. H-bonding can be explained according to two different models: the electrostatic

model and one of the hyperconjugative charge transfer of the lone pair of Y to the H-bonding donor [6–11]. According to the former one, the electron density of Y will attract the proton and consequently the X—H bond will be weakened and simultaneously lengthen, whereas, in the latter one, there is a transfer of electron pair principally the lone pair of Y towards the σ^* X—H orbital inducing a weakening and an elongation of X—H bond upon the formation of the H-bonding. Consequently, a decrease of the corresponding stretching frequency (redshift) and an increase of its infrared intensity are expected to occur. The redshift with rising intensity is characterized as proper H-bonding; it was considered for a long time in several experimental studies as a signature of the H-bond in infrared spectra [12–14]. It was argued that the extent of redshift is depending on the strength of the H-bond [15], the equilibrium distance between the donor and the acceptor [16, 17], and the ionization potential of the proton-acceptor [18]. However, many experimental and theoretical studies revealed the existence of an unusual class of H-bonding [19–31]; this type is characterized as improper H-bond in which the X—H bond contracts while the stretching frequency shifts towards

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higher frequency (blueshift) with reduced infrared intensity. Nevertheless, some exceptions are reported by W. Zierkiewicz et al., who found blueshift with increased infrared intensity in some cases [32, 33]. The blueshift of the stretching frequency of the C—H bond was confirmed experimentally for the first time in 1980 by par Trudeau et al. [34]. Thereafter, many models and hypotheses were reported to explain these phenomena [22–30, 35–39] that will challenge the H-bond notion and determine the most suitable experimental methods used to better detect it such as NMR and IR spectroscopies [40, 41]. Often, the centre of the H-bond (X) is a carbon atom but it can also be another atom as Si, N, P, and F [42–46] or rare gas [47–49]. Among the first reported elucidations to explain the improper H-bonding phenomenon was the one introduced by Hobza et al.; they have proved, by examining the donor-proton behavior in the electric field generated by the point charges of the proton-acceptor, that the formation of H-bond is due to the negative derivative of the dipole moment with respect to the elongation coordinate ($d\mu^\circ/dr_{XH}$) [50]. In addition, Li et al. [42] have proposed that the contraction of the C—H bond causing the blueshift is produced by the short-range repulsive interaction of Pauli between the proton donating and the proton-acceptor. Based on NBO analyses, Hobza and coworkers have proved that in improper H-bonding there is a transfer of a large part of the electron density towards the remote part (orbitals of other atoms bonded to X) of proton donating and only a small part is transferred to the σ^* antibonding orbital of X—H bond. Hence, the geometry of the proton donating is reorganized, leading the contraction of the X—H bond, while, in proper H-bonding, the electron density is almost completely transferred to the σ^* antibonding orbital of X—H bond which becomes weaker and elongate resulting in the redshift of X—H bond stretching frequency [30, 31, 51]. In accordance with the theory suggesting that there are no fundamental discrepancies between proper and improper H-bonding [52–55], Alabugin et al. have established using the NBO (natural bond orbital) analyses that the length of the X—H bond is controlled by the equilibrium of two competitive forces reacting into opposing directions. The X—H elongation due to the charge transfer by hyperconjugation $n(Y) \rightarrow \sigma^*X-H$ is balanced by the contraction of the X—H bond due to the rehybridization (enhancement of the s-character of the hybrid orbital of the atom X) and the polarization of the X—H bond [56–58]. Therefore, two options are possible; if the hyperconjugation predominates, a redshifted stretching frequency of X—H bond will occur; if the rehybridization prevails, a blueshifted stretching frequency will occur [57]. However, Joseph and Jemmis [59] provide a unified explanation based on two competing factors that influence the X—H bond length in X—H \cdots Y systems, it is based on the electrostatic interactions. On the one hand, in the

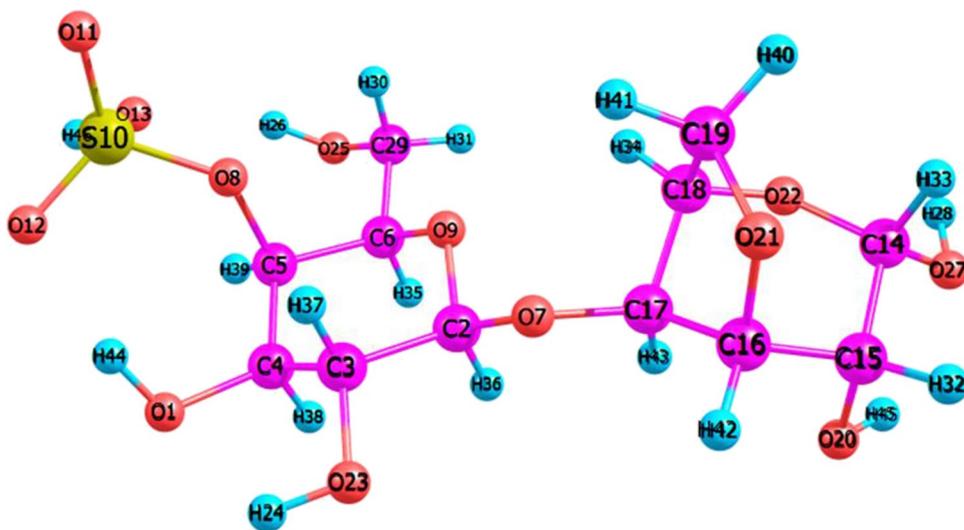
presence of Y and due to the electron affinity of X, there is a gain of electron density at the X—H bond. This leads to the contraction of X—H bond, while the attractive interaction between the electron-deficient H and Y which is rich in electrons leads to the elongation of the X—H bond. The balance between these counteracting forces is decisive on whether the X—H bond stretching frequency is blue- or redshifted [59]. It is interesting to note that according to Grabowski [60], it is possible to differentiate between proper and improper H-bonding by analyzing the position of the critical point of the X—H bond by using the quantum theory of atoms in molecules (QTAIM).

In this paper, we focus our interest on investigating the nature of H-bonds (intramolecular and/or intermolecular) in κ -carrabiose: 4-O-sulfated- β -D-galactopyranosyl (1 \rightarrow 4) 3,6 anhydro- α -D galactopyranose in its neutral form and in the complexes of κ -carrabiose \cdots Y (Y = HF, HCl, HBr, NH₃, H₂O, and H₂S). This disaccharide is one of the two repeating units constituting κ -carrageenan which consists of a linear polysaccharide abundantly used as a texturing agent for various applications in food, chemical, and pharmaceutical industries. This is due to its physical property to form thermoreversible gels [61]. The flexible nature of this disaccharide is due to the important number of hydroxyl groups which confers to it the capacity to be involved in intramolecular H-bonds or intermolecular H-bonds with the neighboring ions or molecules. The chemical structure of the κ -carrabiose as well as atoms numbering are depicted in Fig. 1.

Methods and computational details

At first, full geometry optimizations followed by harmonic frequencies calculation and NBO analyses for the isolated κ -carrabiose were performed by using three global hybrids: B3LYP [62], PBE0 [63, 64], and M06-2X [65] combined with 6-311G** basis set. It was found by previous studies of blueshifting H-bond that the B3LYP/6-311G** model is able to compute correctly this property [66–69]. We have proved in a previous paper that the hybrid-GGA PBE0 had best described the equilibrium distances [70] and the M06-2X which is Truhlar and Zhao functional that performed well for non-covalent interactions [71]. To simulate the solvent effect (water) on H-bonds, we have used the polarizable continuum model (PCM). Subsequently, the donating H-bond κ -carrabiose was optimized in presence of different H-bonds acceptors (Y = HF, HCl, HBr, NH₃, H₂O, and H₂S) using the CBS-4 M method [72, 73]. This latter uses nonlinear natural orbital extrapolation to the complete basis set limit which allows us to avoid the basis set superposition error (BSSE) that can affect the equilibrium distances as was found by the previous paper [74]. The NBO analyses were carried out at

Fig. 1 Structure of κ -carrabiose in its neutral form



the theoretical level MP2/6-311G**. All of the calculations were performed in the Gaussian program [75].

Results and discussion

κ -carrabiose

The first objective of our study is the identification of the intramolecular H-bonds (proper or improper) in κ -carrabiose basing on a simple criterion which is H-bonding distances ($X-H\cdots Y$) cutoff between the proton donating and the acceptor [76]. According to Huang et al., all $X-H\cdots Y$ distances less than 2.80 Å are an indication of a possible H-bond. In κ -carrabiose, the C—H bond is the donating of the proton and the oxygen atom is the proton-acceptor (see Fig. 1).

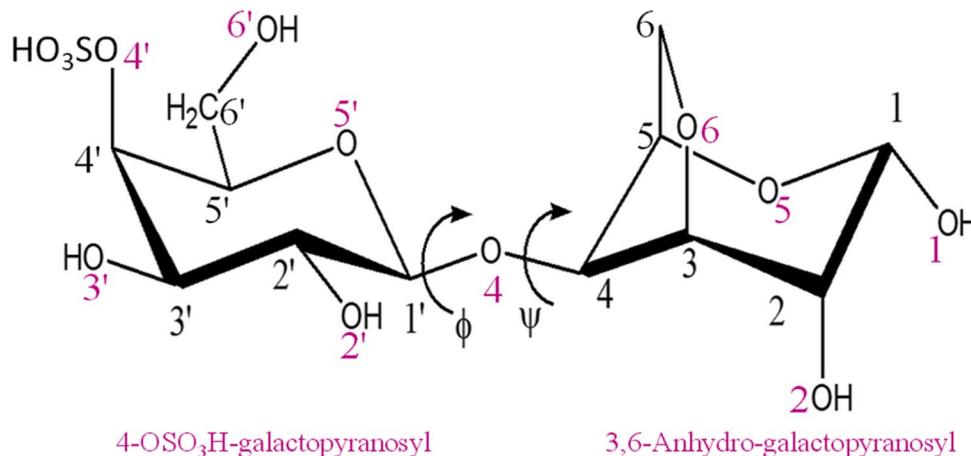
Structure and harmonic vibration analyses

All possible C—H \cdots O distances in κ -carrabiose computed using the global hybrids B3LYP, PBE0, and M06-2X combined with 6-311G** basis set are presented in Table 1 in Supporting Information. The results reveal that there is 39 C—H \cdots O H-bonds and all of them are less than 2.80 Å. We distinguish two types of H-bonds; 38 intra-residue either the 4-O-sulfated-galactopyranosyl unit or the 3,6-anhydro-galactopyranosyl unit and 1 inter-residue (Fig. 2).

In order to determine which global hybrid has correctly reproduced the infrared spectrum of κ -carrabiose, we have compared the calculated frequencies to those observed experimentally for κ -carrageenan [77, 78].

Indeed, the experimental spectrum has served as a basis to get an approximate idea of the vibration region of the C—H bonds in the disaccharide, because we know that the polysaccharide is a repetition of the κ -carrabiose unit. Furthermore, this polygalactane is arranged as a double helix

Fig. 2 κ -carrabiose; 4-O-sulfated- β -D-galactopyranosyl (1 \rightarrow 4) 3,6-anhydro- α -D-galactopyranose



bonded by well-defined H-bonds which can influence the elongation frequencies of the C—H bond. When comparing to the experimental spectrum in which the characterized C—H bond vibrations are visible in the 2802–3028 cm⁻¹ region, we found that the theoretical spectrum obtained from the hybrid-GGA functional PBE0 is closer to the experimental one in which the assigned C—H bond vibrations are found between 2854 and 3078 cm⁻¹, whereas for both other functionals the C—H stretching frequencies are presented in 2947–3152 cm⁻¹ and 3009–3168 cm⁻¹ regions when B3LYP and M06-2X functionals are used, respectively (cf. Figure 1 in Supporting Information). Therefore, we opted for the global hybrid PBE0 functional to perform further calculations in this part of the work.

NBO analyses

As noted earlier, according to Hobza and coworkers [30, 31, 60], an improper H-bond can be formed throughout the electron transfer of “n” lone pair electron of the proton-acceptor (Y) towards the isolated part rather than the $\sigma^*(\text{X—H})$ antibonding orbital of the proton donating.

The charge transfer or interaction between occupied Lewis NBO orbitals (donors) and unoccupied non-Lewis NBO orbitals (acceptors) $n(\text{Y}) \rightarrow \sigma^*\text{X—H}$ is expressed by the stabilization energy $E(2)$ computed by the second-order perturbation using NBO methods [79–82] introduced in Gaussian 09 program. For each NBO donor (i) and acceptor (j), $E(2)$ is given by Eq. (1):

$$E(2) = -q_i \frac{F_{ij}^2}{\epsilon_j^{(L)} - \epsilon_j^{(NL)}} \quad (1)$$

F_{ij}^2 is the Fock matrix element between i and j NBO orbitals, $\epsilon_j^{(L)}$ and $\epsilon_j^{(NL)}$ are, respectively i and j NBO orbital energies, and q_i is the population of the donating i orbital.

In our case, the hyperconjugative charge transfer $n(\text{Y}) \rightarrow \sigma^*\text{X—H}$, $E(2)$ is computed between the p orbital (lone pair) of oxygen and antibonding $\sigma^*\text{C—H}$ bond or antibonding orbitals of the isolated part, in other word non-participating orbitals in H-bond formation.

Thus, to identify which C—H...O distances (cf. Table 1 in Supporting Information) represent a possible H-bond, we performed NBO analyses at the theoretical level PBE0/6-311G**, the corresponding results are summarized in Table 2 in Supporting Information. According to $E(2)$ values, only 16 C—H...O distances exhibit a charge transfer towards the antibonding $\sigma^*\text{C—H}$ bond or towards the isolated part (cf. Table 2 in Supporting Information). Therefore, we can affirm an H-bonding network exists (see Fig. 3) without being able to distinguish the nature of the H-bonds as proper or improper.

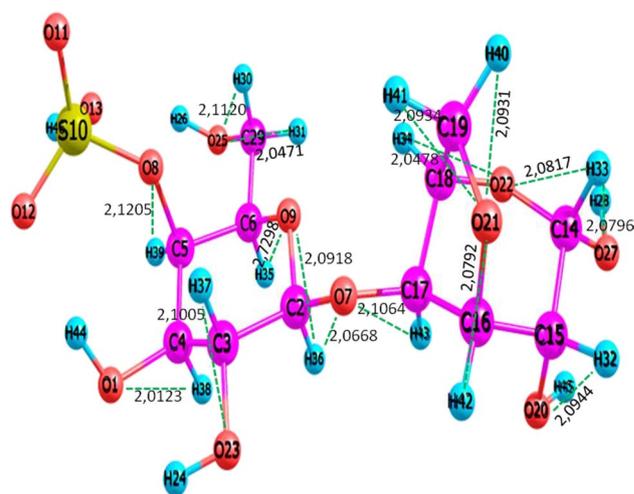


Fig. 3 H-bonding network in isolated κ -carrabiose computed at the PBE0/6-311G** level of theory

Table 1 Variation of C—H distances $\Delta r(\text{C—H})$ in Å, elongation frequencies $\Delta \nu(\text{C—H})$ in cm⁻¹, and IR intensities ΔI in km mol⁻¹ characterizing the (C—H) bonds obtained by the PBE0/6-311G** calculation

H-bond	$\Delta r(\text{C—H})^{[a]}$	$\Delta \nu(\text{C—H})^{[a]}$	$\Delta I^{[a]}$
C ₍₁₄₎ —H ₍₃₃₎ ...O ₍₂₇₎	-0.0014	10	36
C ₍₁₅₎ —H ₍₃₂₎ ...O ₍₂₀₎	-0.0009	9	24
C ₍₁₆₎ —H ₍₄₂₎ ...O ₍₂₁₎	-0.0006	-9	18
C ₍₁₇₎ —H ₍₄₃₎ ...O ₍₇₎	0.0030	-1	10
C ₍₁₈₎ —H ₍₃₄₎ ...O ₍₂₂₎	-0.0016	0	1
C ₍₁₉₎ —H ₍₄₀₎ ...O ₍₂₁₎	-0.0010	6	30
C ₍₁₉₎ —H ₍₄₁₎ ...O ₍₂₁₎	-0.0008	9	16
C ₍₂₎ —H ₍₃₆₎ ...O ₍₇₎	-0.0019	23	40
C ₍₃₎ —H ₍₃₇₎ ...O ₍₂₃₎	-0.0003	1	37
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	-0.0020	22	12
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	-0.0007	8	2
C ₍₆₎ —H ₍₃₅₎ ...O ₍₉₎	-0.0024	25	16
C ₍₂₉₎ —H ₍₃₁₎ ...O ₍₂₅₎	0.0002	-2	21
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	0.0000	1	19

^[a]These results represent the differences between the solvated and isolated κ -carrabiose

Among 16 bonds, 14 have suffered changes upon the solvation

In order to get more details on the H-bonding network and to verify if the disaccharide will be affected by the aqueous medium, we have implicitly solvated the κ -carrabiose using the polarizable continuum model (PCM). It is expected, in a structural point of view, for the κ -carrabiose which is a flexible molecule as other similar disaccharides [74, 83–85] that its conformation may be influenced by hydration, namely the explicit one. Table 1 reports differences between solvated and isolated

κ -carrabiose corresponding to C—H bonds (only those affected by the solvent) distances, stretching mode frequencies, and the corresponding infrared intensities computed at the PBE0/6-311G** level of theory. We have also carried out parallel analog calculations using B3LYP and M06-2X functionals which yielded very close results (cf. Table 3 in Supporting Information).

After analyzing Δr values, we observe that almost all of C—H bonds are contracted (the most significant values are noted for $C_{(14)}\text{---}H_{(33)}$, $C_{(18)}\text{---}H_{(34)}$, $C_{(2)}\text{---}H_{(36)}$, $C_{(4)}\text{---}H_{(38)}$, and $C_{(6)}\text{---}H_{(35)}$ bonds corresponding to $\Delta r(\text{C—H}) = -0.0014, -0.0016, -0.0019, -0.0020,$ and -0.0024 Å, respectively) upon the solvation causing blueshifted stretching frequencies of C—H bonds with $\Delta\nu = 10, 23, 22,$ and 25 cm^{-1} , corresponding to $C_{(14)}\text{---}H_{(33)}$, $C_{(2)}\text{---}H_{(36)}$, $C_{(4)}\text{---}H_{(38)}$, and $C_{(6)}\text{---}H_{(35)}$, respectively. The exception was noted for the $C_{(18)}\text{---}H_{(34)}$ bond which did not show any shift of vibrational frequency ($\Delta\nu = 0$) (see Table 1). Such shifts accompanied by the contraction of (C—H) bond lengths can be considered as an indicator of improper-H bond formation although the fact that the intensities of the corresponding bonds increased. A similar result was obtained by W. Zierkiewicz et al. for enflurane \cdots acetone complexes [32, 33].

According to the standard H-bond mechanism described by Reed et al. [58], the redshift of the H-bond is produced upon the elongation of the X—H bond accompanied by a decrease of the corresponding stretching. In our case, the only two stretching modes of C—H bonds were found for $C_{(17)}\text{---}H_{(43)}$ and $C_{(29)}\text{---}H_{(31)}$ for which $\Delta r = 0.0030$ and 0.0002 Å, respectively; they are accompanied by a very slight decrease of vibrational frequencies ($\Delta\nu = -1$ and -2 cm^{-1}) and an increase of intensities ($\Delta I = 10$ and 21 km mol^{-1} for $C_{(17)}\text{---}H_{(43)}$ and $C_{(29)}\text{---}H_{(31)}$, respectively). Therefore, these two H-bonds can be defined as proper H-bonds.

κ -carrabiose \cdots Y complexes

In this part of the work, we have focused our interest on the study of H-bonds, particularly the improper ones in κ -carrabiose \cdots Y complexes (Y = HF, HCl, HBr, NH₃, H₂O, and H₂S). Considering that the blueshift of H-bonds is a long-range phenomenon [86], all H-bonds acceptors Y were placed at $C_{(18)}\text{---}H_{(34)}\cdots Y$ distance = 3 Å and the α intramolecular angle = $C_{(18)}\text{---}H_{(34)}\cdots F$ (or Cl, Br, N, O, and S) = 180°; afterwards, all obtained systems were preoptimized using HyperChem program [87]. We opted for $C_{(18)}\text{---}H_{(34)}$ bond because it possesses the largest blueshifted stretching frequency (cf. Figure 2 in Supporting Information) and it also showed a significant $C_{(18)}\text{---}H_{(34)}$ contraction; $\Delta r C_{(18)}\text{---}H_{(34)} = -0.0016$ Å (see Table 1) which gives it the possibility to be involved in improper H-bond with the neighboring H-bond acceptors.

Structure and energy analyses

Structure and energy analyses of the complexes fully optimized by using the CBS-4 M method are summarized in Table 2. When analyzing the intermolecular distances of the first group containing hydrogen halide complexes and taking into account the basicity order (HF is more basic than HCl which is itself more basic than HBr) of H-bond acceptors (more the acceptor is basic more it is a good proton-acceptor), we found that $R(Y\cdots H)$ distance becomes shorter when the proton-acceptor becomes more basic. The shortest distance is obtained for hydrogen fluoride for which $R(F\cdots H) = 2.4216$ Å.

It is also important to note that the equilibrium distances variation does not change monotonously. The $R(Y\cdots H)$ distance decreases from κ -carrabiose \cdots FH ($R = 2.4216$ Å) to κ -carrabiose \cdots ClH ($R = 3.8118$ Å), while it increases for κ -carrabiose \cdots BrH complex ($R = 3.2769$ Å), although we expected the opposite fact. A similar behavior was also found out in a previous study reported by Zierkiewicz et al. for $\text{CHX}_3\cdots\text{OH}_2$ (X = F, Cl, Br, and I) complexes [14].

Table 2 Variation of C—H distances $\Delta r(\text{C—H})$ in Å, elongation frequencies $\Delta\nu(\text{C—H})$ in cm^{-1} , the IR intensities ΔI in km mol^{-1} , the equilibrium distances $R(Y\cdots H)$ in Å, and interaction energies

Complex	$\Delta r(\text{C—H})^{[a]}$	$\Delta\nu(\text{C—H})^{[a]}$	$\Delta I^{[a]}$	$R(Y\cdots H)$	ΔE_{int}
κ -carrabiose \cdots FH	-0.0040	56	-5	2.4216	-4.43
κ -carrabiose \cdots ClH	-0.0008	11	-5	3.8118	-0.17
κ -carrabiose \cdots BrH	-0.0015	20	-6	3.2769	-1.28
κ -carrabiose \cdots NH ₃	-0.0028	40	-4	2.6781	-1.57
κ -carrabiose \cdots OH ₂	-0.0035	49	-4	2.4750	-1.89
κ -carrabiose \cdots SH ₂	-0.0007	11	-6	3.6765	-2.65

ΔE_{int} in kcal mol^{-1} characterizing the $(C_{(18)}\text{---}H_{(34)})$ bond obtained by the CBS-4 M method

^[a]These results represent the differences between the complexes and the isolated κ -carrabiose

It should also be mentioned that the interaction energies (ΔE_{int}) are in good agreement with the intermolecular distances; in other words, the longer the $R(Y\cdots H)$ distance, the weaker the interaction ($\Delta E_{\text{int}} = -4.43, -0.17,$ and -1.28 kcal mol $^{-1}$, corresponding to $R(Y\cdots H) = 2.4216, 3.8118,$ and 3.2769 Å for κ -carrabiose \cdots FH, κ -carrabiose \cdots ClH, and κ -carrabiose \cdots BrH, respectively (see Table 2).

Furthermore, when considering the $\Delta r(C\text{---}H)$ values, it is clear that all C—H bonds are contracted upon the complexation. In addition, the variation of C—H distances is chaotic when passing from the κ -carrabiose \cdots FH complex to κ -carrabiose \cdots BrH complex and an anomaly is also observed for the κ -carrabiose \cdots ClH complex, $\Delta r(C\text{---}H) = -0.0040, -0.0008,$ and -0.0015 Å for κ -carrabiose \cdots FH, κ -carrabiose \cdots ClH, and κ -carrabiose \cdots BrH complexes, respectively (Table 2). According to Zierkiewicz et al. [14], the contraction of X—H upon the formation of a complex may be generalized and used as the surest way to predict without ambiguity the blueshift, even without the need to do the frequency calculations which are expensive in terms of CPU time.

We note also that the interaction energies are proportional to the basicity of the hydrogen halide (the stronger the H-bonding acceptor, the important the interaction energy), apart from the anomaly observed for HCl. Actually, it can be clearly highlighted, the correlation between the interaction energies and the contraction of the $C_{(18)}\text{---}H_{(34)}$ bond; in other words, the stronger the interaction is, the important the contraction (see Table 2).

For the second group of complexes (κ -carrabiose \cdots NH $_3$, κ -carrabiose \cdots OH $_2$, and κ -carrabiose \cdots SH $_2$), it is obvious that the variation of the intermolecular distances $R(Y\cdots H)$ are in correlation with C—H bond variations, that means that the shorter the $R(Y\cdots H)$ equilibrium distance, the most important the C—H bond contraction. Indeed, we have $R(N\cdots H) = 2.6781,$ $R(O\cdots H) = 2.4750,$ and $R(S\cdots H) = 3.6765$ Å corresponding to $\Delta r(C\text{---}H) = -0.0028, -0.0035,$ and -0.0007 Å, respectively. The same behavior was also found for the hydrogen halide complexes.

On the other hand, concerning the interaction energies, it is obvious that these latter are inversely related to the H-bonding acceptors' basicity (NH $_3$ more basic than H $_2$ O which is itself more basic than SH $_2$) that is to say the weaker the proton-acceptor (less basic), the stronger the interaction, $\Delta E_{\text{int}} = -1.57, -1.89,$ and -2.65 kcal mol $^{-1}$, corresponding to κ -carrabiose \cdots NH $_3,$ κ -carrabiose \cdots OH $_2,$ and κ -carrabiose \cdots SH $_2$ (see Table 2). This is because H $_2$ S is a better electron-donor than H $_2$ O which is a better electron-donor than NH $_3,$ which will, therefore, strengthen the interaction.

Harmonic vibration analyses

At first, the harmonic vibration analyses results of the six complexes reveal that the stretching frequencies of the $C_{(18)}\text{---}H_{(34)}$ bond of all complexes shift towards high frequencies (blueshift) with the lowest intensities upon the formation of the H-bond.

Else, when considering the basicity order of both H-bonding acceptor groups and the variation of stretching frequencies, it seems that there is a correlation between the blueshifts and the basicity (more basic the proton-acceptor more the important the blueshift). However, this variation is not regular in the second group when we go from κ -carrabiose \cdots NH $_3$ to κ -carrabiose \cdots OH $_2,$ $\Delta\nu = 40,$ and 49 cm $^{-1}$, respectively. This is likely due to the contraction of the C—H bond which is more important in presence of H $_2$ O $\Delta r(C\text{---}H) = -0.0028$ and -0.0035 Å, for κ -carrabiose \cdots NH $_3$ and κ -carrabiose \cdots OH $_2$ complexes, respectively. Then, it seems that a correlation exists between the contraction of the $C_{(18)}\text{---}H_{(34)}$ bond and the extent of the blueshift (see Fig. 4). Besides that, the most important blueshift value is found for hydrogen fluoride complex (κ -carrabiose \cdots FH) with $\Delta\nu = 56$ cm $^{-1}$ and an intensity difference $\Delta I = -5$ km mol $^{-1}$.

Finally, we conclude that it is obvious that there is a relationship between the blueshift and the C—H length, the equilibrium distance ($Y\cdots H$), and the interaction energy; otherwise, the stronger the interaction, the shorter the equilibrium distance $R(Y\cdots H)$ and more the C—H bond contracts causing a more important blueshift (Fig. 4). This result is in good agreement with a previous study reported by Špirko and Hobza [88] for benzene \cdots X complexes (X = benzene, anthracene, and ovalene).

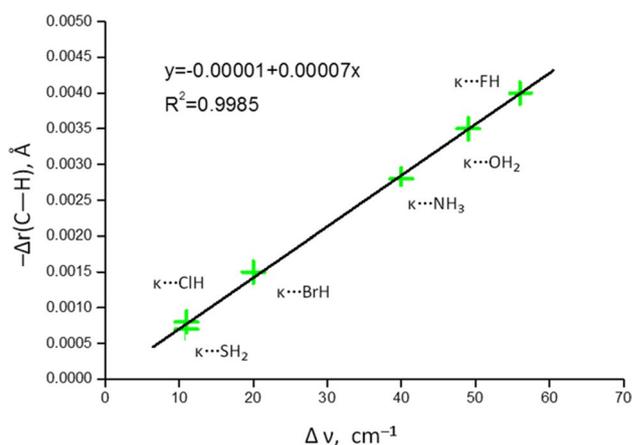


Fig. 4 Correlation between the $C_{(18)}\text{---}H_{(34)}$ bond contraction and the elongation frequencies variation $\Delta\nu$ computed by the CBS-4 M method

NBO analyses

As it was noted above, all κ -carrabiose...Y complexes reveal a blueshift compared to the isolated κ -carrabiose. To distinguish the origin of this shift, NBO analyses were carried out for the optimized structures of complexes and the isolated κ -carrabiose at the theoretical level MP2/6-311G**. The results corresponding to $C_{(18)}\text{---}H_{(34)}$ bond polarization, the NBO electron density difference (ED) of the antibonding orbital $\sigma^* C_{(18)}\text{---}H_{(34)}$, the global electron density transfer (EDT), and the H-bonding index (H-index), the s-character change in the hybrid orbital of the carbon atom of $C_{(18)}\text{---}H_{(34)}$ bond, and the second-order interaction energy $E(2)$ are depicted in Table 3.

First, the (EDT) values listed in Table 3 show that there is a charge transfer between the donor and the acceptor of the proton and that the most important global electron density transfer is obtained for the κ -carrabiose...FH for which EDT = 0.03038 e.

On the one hand, according to Hobbs et al. [30, 31, 51], an improper H-bond can be formed upon the electron density transfer (EDT) from Y towards the remote part of the proton-donor (rather than the antibonding orbital $\sigma^* X\text{---}H$ in the case of proper H-bond) which will consequently contract the $X\text{---}H$ bond and lead to a blueshift of stretching frequency of $X\text{---}H$ bond.

In our case when considering the stabilization energy values $E(2)$ shown in Table 3, it can be clearly seen that there is no hyperconjugative charge transfer of the Y lone pair (n) towards the anti-bonding orbitals σ^* of $C_{(18)}\text{---}H_{(34)}$ bond ($n(Y) \rightarrow \sigma^* C_{(18)}\text{---}H_{(34)}$) for κ -carrabiose...ClH, κ -carrabiose...BrH, and κ -carrabiose...SH₂ complexes, and even when it occurs, it is insignificant (for the κ -carrabiose...NH₃, κ -carrabiose...OH₂, and

κ -carrabiose...FH complexes). Moreover, it was noted a decline of the electron density (ED) on antibonding orbitals $\sigma^*(C\text{---}H)$ upon the formation of the H-bond. This result is consistent with the $E(2)$ and EDT values. Then, it can be affirmed that the major part of the electron density is transferred to the remote part of the proton-donor and that the carrabiose...Y complexes do not possess hyperconjugation interactions and when they exist they are relatively weak, that is, non-dominant. This means that just a little portion of the electron density is transferred to $\sigma^*(C_{(18)}\text{---}H_{(34)})$ orbital.

Nevertheless, the global electron density transfer (EDT) values show that the important part of the electron density is transferred to the remote part of κ -carrabiose rather than the $\sigma^*(C_{(18)}\text{---}H_{(34)})$ bond which is verified by the computed $E(2)$ values between the lone pairs of the proton acceptors and the $\sigma^*(X\text{---}H)$ antibonding orbitals of the isolated part of the proton-donor (cf. Table 4 in Supporting Information).

It is also important to note that hyperconjugation interaction (charge transfer of the lone pair of proton-acceptor towards the proton-donor $n(Y) \rightarrow \sigma^* C_{(18)}\text{---}H_{(34)}$) appeared and gradually increased when the H-bonding acceptors' basicity raised (NH₃ is more basic than H₂O which is more basic than HF). We have, $E(2) = 0.37$, (0.08, 0.32), and 0.07 kcal mol⁻¹ for κ -carrabiose...NH₃, κ -carrabiose...OH₂, and κ -carrabiose...FH complexes, respectively (Table 3).

According to the concept proposed by Alabugin et al. [57], $X\text{---}H$ bond contraction is due to the rehybridization effect, which means the increase of the s-character of the hybrid orbital of X atom as well as the polarization of this bond, when $X\text{---}H$ bond elongation, is due to the hyperconjugation interaction. If the first effect dominates, the $X\text{---}H$ bond becomes shorter and stronger and

Table 3 $C_{(18)}\text{---}H_{(34)}$ bond polarization $\sigma(C\text{---}H)$ Pol, the NBO electron density difference (ED) of the $\sigma^* C_{(18)}\text{---}H_{(34)}$, the global electron density transfer (EDT) in e as well as the H-bonding index (H-index), the s-character variation $\Delta\%$ s-charact in the hybrid orbital

Complex	$\sigma(C\text{---}H)$ Pol		Δ DE $\sigma^*(C\text{---}H)^{[b]}$	EDT	H-index	$\Delta\%$ s-charact ^[b]	$E(2)$
	%C	%H					
	59,79 ^[a]	40,21 ^[a]					
κ -carrabiose...FH	38.88	61.12	-0.00139	0.03038	-0.05	0.92	0.07
κ -carrabiose...ClH	59.92	40.08	-0.00020	0.00177	-0.11	0.22	—
κ -carrabiose...BrH	60.13	39.87	-0.00048	0.00472	-0.10	0.32	—
κ -carrabiose...NH ₃	61.10	38.90	-0.00055	0.00059	-0.93	0.97	0.37
κ -carrabiose...OH ₂	61.16	38.84	-0.00061	0.00545	-0.11	0.96	0.08 ^[c] , 0.32 ^[d]
κ -carrabiose...SH ₂	60.16	39.84	-0.00058	0.00894	-0.06	0.36	—

^[a]% of electron density on C and H atoms of $C_{(18)}\text{---}H_{(34)}$ bond in the isolated κ -carrabiose

^[b]These results represent the differences between the complexes and the isolated κ -carrabiose

^{[c],[d]}Correspond, respectively to n(1) and n(2) oxygen lone pairs

of the carbon atom of $C_{(18)}\text{---}H_{(34)}$ bond and the second-order interaction energy $E(2)$ (kcal mol⁻¹) between Y lone pair (n) and $\sigma^* C_{(18)}\text{---}H_{(34)}$ computed at the MP2/6-311G** level of theory

consequently a blueshift of the stretching frequencies. While the second effect prevails, X—H bond will be lengthened and becomes weaker and results in a redshift of X—H bond frequencies.

Regarding the *s*-character differences ($\Delta\%$ *s*-character between the H-bonding donor and the complex) of the carbon atom of $C_{(18)}\text{---}H_{(34)}$ bond, it is noticed obviously that there is an increase of the *s*-character upon the formation of the complexes. Besides, this rise, as noted above, is accompanied by a contraction of the $C_{(18)}\text{---}H_{(34)}$ bond. It would seem that there is a correlation between the *s*-character and the contraction of the $C_{(18)}\text{---}H_{(34)}$ bond, although this correlation is chaotic (see Fig. 5). It is clear that rehybridization dominates compared to the hyperconjugation effect.

As expected, the rehybridization is proportional to the basicity of the H-bond acceptors. Indeed, the more basic the H-bond acceptor, the more important the $\Delta\%$ *s*-character difference on the carbon atom of $C_{(18)}\text{---}H_{(34)}$ bond

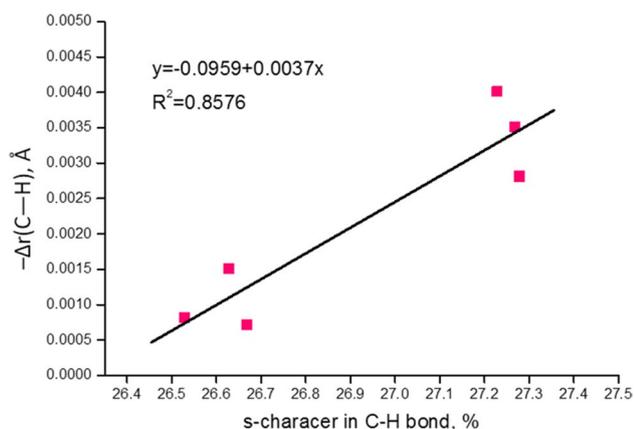


Fig. 5 Correlation between the $C_{(18)}\text{---}H_{(34)}$ bond contraction and the *s*-character on carbon atom computed at the MP2/6-311G** level of theory

between the complex and H-bond donor, except for the hydrogen chloride. We have $\text{NH}_3 > \text{H}_2\text{O} > \text{HF} > \text{H}_2\text{S} > \text{HCl} > \text{HBr}$ corresponding respectively to $\Delta\%$ *s*-character = 0.97, 0.96, 0.92, 0.36, 0.22, 0.32.

Regarding the polarization, when analyzing the electron density distribution on hydrogen and carbon atoms of the $C_{(18)}\text{---}H_{(34)}$ bond, we find that the electron density on each atom becomes more asymmetric during the formation of the H-bond. In other words, the $C_{(18)}\text{---}H_{(34)}$ bond becomes more polarized inducing its contraction.

In order to determine the polarization direction of the $C_{(18)}\text{---}H_{(34)}$ bond, we have evaluated the differences of natural atomic charges on the atoms implied in $C_{(18)}\text{---}H_{(34)}\cdots Y$ bond ($Y = \text{F}, \text{Cl}, \text{Br}, \text{N}, \text{O}, \text{and S}$) between the complexes and the isolated κ -carrabiose. The results are reported in Table 4.

In fact, the polarization of the $C_{(18)}\text{---}H_{(34)}$ bond is due to the decrease of the positive charge on the carbon atom and the concomitant increase of the positive charge on the hydrogen atom and negative charge on the H-bonding acceptor. This was verified for all complexes except the κ -carrabiose $\cdots\text{ClH}$ and κ -carrabiose $\cdots\text{BrH}$. For these latter cases, a decrease of the negative charge on the proton-acceptor is observed, producing moderate contractions ($\Delta q_Y = 0.0103$ and 0.0163 e corresponding respectively to $\Delta r(C\text{---}H)$ variations of -0.0008 and -0.0015 Å, for κ -carrabiose $\cdots\text{ClH}$ and κ -carrabiose $\cdots\text{BrH}$ (Table 4). This is due to the fact that HCl and HBr are very bad H-bonding acceptors, but at the same time very good H-bonding donors.

According to Δq values, it is noted that the more the H-bonding center (carbon atom) negative, the more hydrogen positive and Y ($Y = \text{F}, \text{Cl}, \text{Br}, \text{N}, \text{O}, \text{and S}$) more negative, more the $C_{(18)}\text{---}H_{(34)}$ bond shortens.

Table 4 Differences of natural atomic charges in e on C and H atoms as well as the variation of $C_{(18)}\text{---}H_{(34)}$ distances in Å during the formation of the improper H-bonds in the presence of the different proton-acceptors (1): HF, (2): HCl, (3): HBr, (4): NH_3 , (5): H_2O , and (6): SH_2

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta r(C\text{---}H)^{[a]}$	-0.0040	-0.0008	-0.0015	-0.0028	-0.0035	-0.0007
$\Delta q^{[b]} \text{C}$	-0.0064	-0.0021	-0.0015	-0.0119	-0.0111	-0.0023
$\Delta q^{[b]} \text{H}$	0.0313	0.0069	0.0112	0.0302	0.0311	0.0119
$\Delta q^{[b]} Y$	-0.0702	0.0103	0.0163	-0.0676	-0.0640	-0.482

^[a]These results represent the differences between the complexes and the isolated κ -carrabiose

^[b]These results represent the atomic charge differences upon the complexation on $Y = \text{F}, \text{Cl}, \text{Br}, \text{N}, \text{O}, \text{and S}$ in (1), (2), (3), (4), (5), and (6) proton-acceptors, respectively

Taking into account the electronegativity of each element: F, Cl, Br, N, O, and S, it is very clear that the more the atom is electronegative, the more the contraction is important. In fact, we have $\chi(\text{F})=4$, $\chi(\text{O})=3.5$, $\chi(\text{N})=\chi(\text{Cl})=3$, $\chi(\text{Br})=2.8$, $\chi(\text{S})=2.5$ corresponding, respectively to $\Delta r(\text{C}—\text{H}) = -0.0040, -0.0035, -0.0028, -0.0008, -0.0015$, and -0.0007 \AA (see Fig. 6).

Although the nitrogen and chlorine possess analog electronegativity, the contraction of the $\text{C}_{(18)}—\text{H}_{(34)}$ bond in presence of ammonia is more significant. This is likely due to the fact that NH_3 which is more basic is a better H-bond acceptor than HCl which is more acid.

It is important also to note that the $\text{C}_{(18)}—\text{H}_{(34)}$ bond becomes more polarized (increase of the ionic character) when the s-character increases on the carbon atom of $\text{C}_{(18)}—\text{H}_{(34)}$. A similar conclusion was found by Li et al. [42], Alabugain et al. [57], and Kryachko et al. [89].

In accordance with the subsequently obtained results, all $\text{CH}\cdots\text{Y}$ ($\text{Y} = \text{HF}, \text{HCl}, \text{HBr}, \text{NH}_3, \text{H}_2\text{O},$ and H_2S) bonds are characterized as improper H-bonds.

Another criterion can be used to confirm the results obtained previously; it is the index of H-bond (H-index) proposed by Hobza [90]. This latter is a reliable mean used to characterize the type of H-bond (proper and improper).

According to Hobza, one between two definitions of H-index is to consider it as a ratio of electron density (ED) transferred to $\text{C}—\text{H}$ bond and the global electron density transfer (EDT):

$$\text{H-Index} = \frac{\Delta\sigma^*}{\text{EDT}}$$

$\Delta\sigma^*$ represents the variation of the electron density (ED) in the σ^* antibonding orbital of $\text{C}—\text{H}$ bond and is defined as a difference of electron density (ED) between the isolated

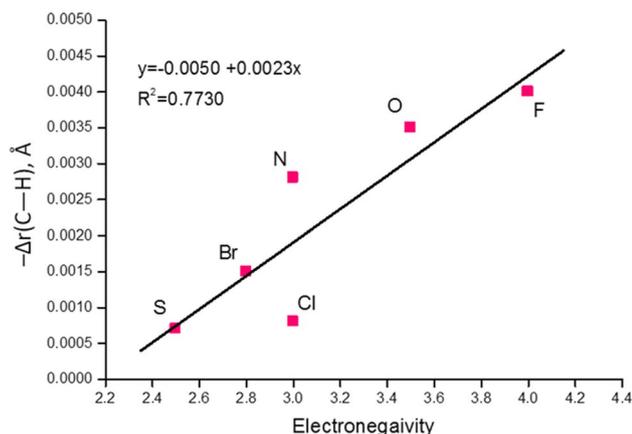


Fig. 6 Correlation between the $\text{C}_{(18)}—\text{H}_{(34)}$ bond contraction and the electronegativity of H-bond acceptor Y ($\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{N}, \text{O},$ and S) computed at the MP2/6-311G** level of theory

system and the complex. EDT represents the global electron density transfer between acceptor and donor of H-bonding.

For proper H-bonding complexes, the H-index values range between 1.0 and 0.7. For the improper H-bonding complexes, the H-index ranges between 0.3 and 0; it also can be negative.

Concerning the six κ -carrabiose $\cdots\text{Y}$ complexes, H-index values reported in Table 3 are all negative; we have H-index = $-0.05, -0.11, -0.10, -0.93, -0.11,$ and -0.06 , for κ -carrabiose $\cdots\text{FH}$, κ -carrabiose $\cdots\text{ClH}$, κ -carrabiose $\cdots\text{BrH}$, κ -carrabiose $\cdots\text{NH}_3$, κ -carrabiose $\cdots\text{OH}_2$, and κ -carrabiose $\cdots\text{SH}_2$, respectively. This means that the major part of electron density is transferred towards the remote part of H-bonding acceptor which leads to the formation of improper H-bonding. These results are in good agreement with previous results which prove that $\text{C}_{(18)}—\text{H}_{(34)}\cdots\text{Y}$ ($\text{Y} = \text{HF}, \text{HCl}, \text{HBr}, \text{NH}_3, \text{H}_2\text{O},$ and H_2S) are all blueshifting H-bonds.

Intramolecular H-bonds in κ -carrabiose $\cdots\text{Y}$ complexes

This part of the paper is devoted to the characterization of intramolecular H-bonds within the formed complexes. We first analyze the $\text{C}—\text{H}$ bonds which are implied in $\text{C}—\text{H}\cdots\text{O}$ H-bonds as well as the stretching frequencies and we end by NBO analyses at the MP2/6-311** level of theory.

Structures and harmonic vibration analyses

After assessing the distance variations of $\text{C}—\text{H}$ bonds of κ -carrabiose depicted in Table 1, almost all of them (9 among 14) have displayed a significant change either through an elongation or a contraction during the formation of κ -carrabiose $\cdots\text{Y}$ complexes (cf. Table 5 in Supporting Information).

Only the three bonds that have displayed a constant $\Delta r(\text{C}—\text{H})$ during the formation of H-bonds in the six complexes will be considered subsequently ($\text{C}_{(4)}—\text{H}_{(38)}$, $\text{C}_{(5)}—\text{H}_{(34)}$, and $\text{C}_{(29)}—\text{H}_{(30)}$). As we have seen previously, these bonds are implied in H-bond with $\text{O}_1, \text{O}_8,$ and O_{25} atoms, respectively. Table 5 reports the variation distances, the stretching frequencies, and the infrared intensities that characterize the $\text{C}—\text{H}$ bonds during the complexation obtained by the CBS-4 M method.

As we noted above, according to Zierkiewicz et al. [14], a blueshift accompanied by a decrease of intensity is due to the contraction of the $\text{C}—\text{H}$ bond, whereas the redshift is due to the elongation of the $\text{C}—\text{H}$ bond accompanied by an increase of intensity.

When analyzing $\Delta r(\text{C}—\text{H})$ values as well as the corresponding $\Delta\nu(\text{C}—\text{H})$ and ΔI , it is obvious that $\text{C}_{(29)}—\text{H}_{(30)}\cdots\text{O}_{(25)}$ bond is a proper H-bond with a

Table 5 Variation of C—H distances $\Delta r(\text{C—H})$ in [Å], elongation frequencies $\Delta \nu(\text{C—H})$ in cm^{-1} , and IR intensities ΔI in km mol^{-1} characterizing the (C—H) bonds obtained by the CBS-4 M method

H-bond	$\Delta r(\text{C—H})^{[a]}$	$\Delta \nu(\text{C—H})^{[a]}$	$\Delta I^{[a]}$	$\Delta r(\text{C—H})^{[a]}$	$\Delta \nu(\text{C—H})^{[a]}$	$\Delta I^{[a]}$	$\Delta r(\text{C—H})^{[a]}$	$\Delta \nu(\text{C—H})^{[a]}$	$\Delta I^{[a]}$
	$\kappa\text{-carrabiose}\cdots\text{FH}$			$\kappa\text{-carrabiose}\cdots\text{ClH}$			$\kappa\text{-carrabiose}\cdots\text{BrH}$		
$\text{C}_{(4)}\text{—H}_{(38)}\cdots\text{O}_{(1)}$	-0.0026	34	-48	-0.0027	35	-48	-0.0027	35	-49
$\text{C}_{(5)}\text{—H}_{(39)}\cdots\text{O}_{(8)}$	-0.0019	31	-4	-0.0023	36	-4	-0.0021	33	-4
$\text{C}_{(29)}\text{—H}_{(30)}\cdots\text{O}_{(25)}$	0.0086	-37	2	0.0079	-72	26	0.0081	-67	18
	$\kappa\text{-carrabiose}\cdots\text{NH}_3$			$\kappa\text{-carrabiose}\cdots\text{H}_2\text{O}$			$\kappa\text{-carrabiose}\cdots\text{SH}_2$		
$\text{C}_{(4)}\text{—H}_{(38)}\cdots\text{O}_{(1)}$	-0.0027	34	-48	-0.0027	34	-49	-0.0027	35	-48
$\text{C}_{(5)}\text{—H}_{(39)}\cdots\text{O}_{(8)}$	-0.0021	33	-4	-0.0020	32	-4	-0.0024	37	-4
$\text{C}_{(29)}\text{—H}_{(30)}\cdots\text{O}_{(25)}$	0.0086	-59	3	0.0090	-48	4	0.0081	-68	15

^[a]These results represent the differences between the complexes and the isolated $\kappa\text{-carrabiose}$

significant elongation $\Delta r(\text{C—H}) = 0.0086, 0.0079, 0.0081, 0.0086, 0.0090,$ and 0.0081 Å, corresponding to a shift towards low vibration frequencies; $\Delta \nu = -37, -72, -67, -59, -48,$ and -68 cm^{-1} , respectively for $\kappa\text{-carrabiose}\cdots\text{Y}$ ($\text{Y} = \text{HF}, \text{HCl}, \text{HBr}, \text{NH}_3, \text{H}_2\text{O},$ and H_2S) complexes. These six redshifts are accompanied by an increase of intensities (see Table 5); the most important intensity variation is obtained for the hydrogen chloride complex ($\Delta I = 26$ km mol^{-1}).

Regarding $\text{C}_{(4)}\text{—H}_{(38)}\cdots\text{O}_{(1)}$ and $\text{C}_{(5)}\text{—H}_{(39)}\cdots\text{O}_{(8)}$ bonds, the contraction of C—H bonds as well as the shifts to higher stretching frequencies and the reduction of their corresponding band intensities indicate clearly that both bonds represent an improper H-bonds.

We also noted that the contraction of $\text{C}_{(4)}\text{—H}_{(38)}$ bond is not affected by the nature of the proton-acceptors; $\Delta r = -0.0026, -0.0027, -0.0027, -0.0027, -0.0026,$ and -0.0027 Å for $\kappa\text{-carrabiose}\cdots\text{FH}, \kappa\text{-carrabiose}\cdots\text{ClH}, \kappa\text{-carrabiose}\cdots\text{BrH}, \kappa\text{-carrabiose}\cdots\text{NH}_3, \kappa\text{-carrabiose}\cdots\text{OH}_2,$ and $\kappa\text{-carrabiose}\cdots\text{SH}_2$ complexes, respectively. The same remark is done for the frequencies and their band intensities since $\Delta \nu = 34, 35, 35, 34, 34,$ and 35 cm^{-1} corresponding to $\Delta I = -48, -48, -49, -48, -49,$ and -48 km mol^{-1} for $\kappa\text{-carrabiose}\cdots\text{FH}, \kappa\text{-carrabiose}\cdots\text{ClH}, \kappa\text{-carrabiose}\cdots\text{BrH}, \kappa\text{-carrabiose}\cdots\text{NH}_3, \kappa\text{-carrabiose}\cdots\text{OH}_2,$ and $\kappa\text{-carrabiose}\cdots\text{SH}_2$ complexes, respectively.

NBO analyses

In order to understand the origin of the significant elongation of the $\text{C}_{(29)}\text{—H}_{(30)}$ bond as well as the contraction of $\text{C}_{(4)}\text{—H}_{(38)}$ and $\text{C}_{(5)}\text{—H}_{(39)}$ bonds, we have analyzed the charge transfer due to the hyperconjugation interactions ($n(\text{O}) \rightarrow \sigma^*(\text{C—H})$) and the s-character of the hybrid orbital in carbon atom of the C—H bonds and their polarization. The NBO analyses of the six complexes

and the isolated $\kappa\text{-carrabiose}$ computed at MP2/6-311G** theoretical level are reported in Table 6.

Initially, the second-order interaction energies for the proper and improper H-bonds do not provide any significant information to differentiate between both types of H-bonds since both possess a charge transfer of the lone pairs of oxygen atom towards the $\sigma^*(\text{C—H})$ antibonding orbital.

However, based on the s-character of the hybrid orbital of the carbon atom of the three bonds, $\Delta\%$ s-charact values show that in both improper H-bonds $\text{C}_{(4)}\text{—H}_{(38)}$ and $\text{C}_{(5)}\text{—H}_{(39)}$, the s-character increases during the complexation: $\Delta\%$ s-charact = (1.27 and 1.21), (1.26 and 1.27), (1.26 and 1.24), (1.23 and 1.22), (1.25 and 1.22), and (1.25 and 1.31) corresponding to $\text{C}_{(4)}\text{—H}_{(38)}$ and $\text{C}_{(5)}\text{—H}_{(39)}$, for $\kappa\text{-carrabiose}\cdots\text{FH}, \kappa\text{-carrabiose}\cdots\text{ClH}, \kappa\text{-carrabiose}\cdots\text{BrH}, \kappa\text{-carrabiose}\cdots\text{NH}_3, \kappa\text{-carrabiose}\cdots\text{OH}_2,$ and $\kappa\text{-carrabiose}\cdots\text{SH}_2$ complexes, respectively.

On the other hand, the s-character is reduced in $\text{C}_{(29)}\text{—H}_{(30)}$ bond during the formation of the proper H-bond, this is verified for all complexes (see Table 6).

Taking into account the polarization, when comparing to the isolated proton-donor, we note that there is no evident relation between the polarization and s-character variation; in other words, the inequitable electron density distribution in C—H bonds has not changed significantly during the formation of H-bonds. We conclude that only the rehybridization of the carbon atom in the C—H bond is the responsible factor of intramolecular H-bonds nature for $\kappa\text{-carrabiose}\cdots\text{Y}$ complexes.

Lastly, it must be highlighted that in both H-bond types (proper or improper), the s-character dominates; it is reflected either by a decrease for proper H-bonds or by an increase for the improper ones.

Table 6 The s-character variation $\Delta\%$ s-charact in the hybrid orbital of the carbon atom of the C—H bond, C—H bond polarization $\sigma(\text{C—H})$ Pol, and the second-order interaction energy $E(2)$ (kcal mol⁻¹) between Y lone pair (*n*) and $\sigma^*\text{C—H}$ bond computed at the MP2/6-311G** level of theory

H-bond	$\Delta\%$ s-charact ^[a]	$\sigma(\text{C—H})$ Pol		$E(2)$ ^[b]	$E(2)$ ^[c]
		%C	%H		
κ-carrabiose...FH					
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	1.27	41.21	58.79	3.89	1.31
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	1.21	39.63	60.37	2.23	—
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	-0.61	42.71	57.29	3.28	1.19
κ-carrabiose...ClH					
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	1.26	58.82	41.18	3.97	1.14
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	1.27	60.49	39.51	2.27	—
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	-0.25	57.69	42.31	3.44	1.16
κ-carrabiose...BrH					
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	1.26	58.82	41.18	3,95	1.16
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	1.24	60.42	39.58	2.25	—
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	-0.34	57.61	42.39	3.38	1.29
κ-carrabiose...NH ₃					
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	1.23	58.77	41.23	3.23	1.38
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	1.22	60.39	39.61	2.24	—
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	-0.56	57.36	42.64	3.93	1.19
κ-carrabiose...OH ₂					
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	1.25	58.79	41.21	3.92	1.23
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	1.22	60.38	39.62	2.23	—
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	-0.68	57.21	42.79	3.24	1,36
κ-carrabiose...SH ₂					
C ₍₄₎ —H ₍₃₈₎ ...O ₍₁₎	1.25	58.81	41.19	3.94	1.27
C ₍₅₎ —H ₍₃₉₎ ...O ₍₈₎	1.31	60.52	39.48	2.28	—
C ₍₂₉₎ —H ₍₃₀₎ ...O ₍₂₅₎	-0.31	57.58	42.42	3.40	1.02

^[a]These results represent the differences between the complexes and the isolated κ-carrabiose

^[b] $E(2)$ between the lone pair (1) and $\sigma^*(\text{C—H})$

^[c] $E(2)$ between the lone pair (2) and $\sigma^*(\text{C—H})$

For the C—H bonds, polarization in the isolated κ-carrabiose (%C and %H)=(58.35 and 41.65), (60.38 and 39.62), and (58.91 and 41.09), for C₍₄₎—H₍₃₈₎, C₍₅₎—H₍₃₉₎, and C₍₂₉₎—H₍₃₀₎, respectively

Conclusion

The purpose of this work was to differentiate between the nature of H-bonds for the κ-carrabiose and its complexes (κ-carrabiose...Y) using quantum mechanics methods.

Firstly, the structure and harmonic vibration analyses of all complexes reveal that the C₍₁₈₎—H₍₃₄₎...Y bond is an improper H-bond where a significant contraction was observed during the formation of a complex which induces, in turn, a significant blueshifted stretching frequency. This type of blueshift is consistent with C—H

bonds contractions, intermolecular equilibrium distances $R(\text{Y...H})$, and interaction energies.

Secondly, NBO analyses have shown the reduction of electron density (ED) on the antibonding orbitals $\sigma^*(\text{C—H})$ during the formation of the H-bond. That fact led us to conclude that the complexes, on the one hand, do not possess hyperconjugative interactions and even when they exist they are weak and do not dominate.

This hyperconjugative interaction (charge transfer of the lone pairs of proton-acceptor towards the proton-donor ($n(\text{Y}) \rightarrow \sigma^*\text{C—H}$) was demonstrated to appear and to

increase gradually when the basicity of H-bonding acceptors is augmented.

Besides, the correlation between the contraction of the $C_{(18)}-H_{(34)}$ bond and the increase of the s-character of the hybrid orbital in carbon atom was verified for all κ -carrabiose $\cdots Y$ complexes upon the formation of the improper H-bonds $C_{(18)}-H_{(34)}\cdots Y$ ($Y = F, Cl, Br, N, O,$ and S).

Additionally, when considering the polarization, it was proved that the more H-bond center (carbon atom in $C_{(18)}-H_{(34)}\cdots Y$) negative, the more hydrogen positive, the more Y negative and the more important the shortening of the $C_{(18)}-H_{(34)}$ bond.

Finally, from NBO analyses, we established that the κ -carrabiose possess the intramolecular H-bonds which are either proper or improper. In this case, the rehybridization of the carbon atom in $C-H$ bonds is responsible for the intramolecular H-bonds nature. If the s-character increases, the H-bond will be improper; if it decreases, the H-bond will be proper; thus, the rehybridization is the dominating force.

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