Intermolecular orbital repulsion effect on the blue-shifted hydrogen bond

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Abstract

This work suggests a possible phenomenon of the blue-shifted hydrogen bond, which is due to the compression caused by two opposite type of interactions in X–H...Y system (Benzene...H–F and T-shaped benzene dimer have been considered as model systems). One type is the attraction between H-bond acceptor and remote part of H-bond donor and the other type is the repulsion between X–H and H-bond acceptor. The results obtained from molecular orbital interactions reveal that the repulsive four-electron-two-orbital interactions between the σX–H orbitals of H-bond donor and the occupied orbitals of H-bond acceptor play an important role towards characterization of blue-shifted hydrogen bond with shortening of the X–H bond.

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1. Introduction

Hydrogen bond plays a crucial role in chemistry, physics and biology [1–3]. In general understanding, hydrogen bond occurs in the X–H...Y system, where the ‘X’ and ‘Y’ are electronegative elements and the ‘Y’ possesses one or more lone pairs. The lone pair electrons delocalize from hydrogen acceptor Y to the σ* orbital of X–H, therefore the X–H bond is weakened and lengthened with a concomitant red-shifted X–H stretching frequency [4]. However, blue shifts of X–H frequencies were detected experimentally [5–8] and worthily enormous number of theoretical studies [9–24] have been reported in last five years, mainly due to pioneering work initiated by Hobza et al. [11]. Blue-shifted hydrogen bonds are specifically relevant in the context of biomolecular interactions. Most of the theoretical studies on such blue-shifting hydrogen-bonded complexes are accounted for C–H...O interactions and the same can also be obtained in few cases for more general X–H...Y system.

In 1998, Hobza et al. [11] have reported a new type binding, improper, blue shifted hydrogen bond with shortening of the C–H bond and a blue-shifted C–H stretching frequency in T-shaped benzene dimer. Later in their review articles [12,13], they have pointed out that the shortening of X–H bond is structural reorganization, a concomitant electron density transfer from proton acceptor Y to remote highly electronegative atoms, X instead of σX–H anti-bonding orbital. In contrast to Hobza et al. views, Scheiner and co-workers [14,15] have examined the interactions in CF₃H₃... O, and they have observed the C–H...O interaction is similar to conventional O–H...O, H-bond in terms of geometric behavior, electron density shifts, and energy component analysis. They have made conclusion that there are no fundamental distinctions between red- and blue-shifted hydrogen bond.

Several other studies have considered the blue-shifted hydrogen bond as the phenomenon due to the electrostatic contributions and the effect of electric field. Masunov and Dannenberg [16] have shown the polarization...
of C–H bond by small electric fields lead to the shifting of electron density from the hydrogen makes the bond shorter and strong. According to Hermansson [17], the reasons for the blue-shifting C–H bonds lie in the sign of the dipole moment derivative with respect to the stretching coordinate combined with electronic exchange overlap at moderate and shorter H-bonded distances. Liu and co-workers [18] have not agreed completely with Hobza et al. and suggested that at the equilibrium geometry, the electrostatic attraction can be balanced by Pauli repulsion; therefore, blue-shifted hydrogen bonds should be a result of repulsive steric interactions [19]. Qian and Krimm [20] have also treated molecules with electric field and analyzed the dynamic properties of the H-bond donor group; the cooperative effect of the external electric field and induced dipole derivatives of the X–H bond become parallel to lengthens and anti-parallel to shortens the X–H bond.

Alabugin et al. [21] have suggested a chemical perspective to explain this phenomenon through Bent’s [22] rule, both in ‘proper’ and ‘improper’ hydrogen bond, the hyperconjugative \( n(Y) \rightarrow \sigma^*(X–H) \) can be balanced by the increase in s-character and polarization of the X–H bond. Liu and co-workers [26] have also noted that rehybridization can not be a generally applicable driving force for the blue-shifted hydrogen bond for F–He–H...Y (Y = N₂, CO and He) systems, since He is incapable of rehybridization.

In this Letter, we would like to report a possible phenomenon of the blue-shifted hydrogen bond, which is due to the compression caused by two opposite type of interactions in X–H...Y system (Benzene...H–F and T-shaped benzene dimer have been considered as model systems). One type is the attraction between H-bond acceptor and remote part of H-bond donor and the other type is the repulsion between X–H and H-bond acceptor. It has also been observed that the role of electrostatic contribution exceeds polarization effect; due to increase in s-character of C–H bond. Moreover, according to the orbital interaction theory [27], the attractive two-electron-two-orbital interactions are balanced by the repulsive forces, four-electron-two-orbital interactions at optimum distance of approach for two neutral molecules separated by van der Waals distance of interaction. The molecular orbital interactions analysis has been employed for our model systems (benzene...F–H and T-shaped benzene dimer).

2. Computational method

The second-order Möller-Plesset (MP2) method has been employed in our calculation so as to include electron correlation explicitly in order to obtain good representations of dispersion and electrostatic forces that are responsible for the binding of the species. Valence triple-zeta basis set with polarization function, 6-311G (2d, p) is used in the overall calculations. Earlier, Tsuzuki et al. [28] have also used the valence-triple-zeta basis set with polarization function for the intermolecular interaction energy of T-shaped benzene dimer, compared to valence double-zeta basis set used by Hobza et al. MP2 densities are used in natural bond orbital (NBO) analysis [4,29]. The benzene monomer is optimized at D₆h symmetry and both the systems: benzene...F–H and the T-shaped benzene dimer are optimized with constrained at C₂ᵥ symmetry. The binding energies are corrected for basis set superposition errors (BSSE) by means of counterpoise method [30]. All calculations including NBO have been performed with GAUSSIAN 98 [31] suite of program. Moreover, the benzene...F–H system has been optimized with two different kinds of constraint intermolecular distance: firstly with the fixed H...F distance ranging from 2.4 to 5.0 Å and secondly with the fixed C...F distance in which the residual coordinates has been optimized. For those calculations with constraint distance, the results are accepted only for the energy derivatives, \( dE/dr_{C–H} \) are found to be less than 5 × 10⁻³.

3. Results and discussion

Table 1 depicts the optimized C–H bond length, intermolecular distance, interaction energies, and results obtained from NBO analysis for benzene monomer, benzene...F–H and T-shaped benzene dimer. It can be observed that the C–H bond length has been found to decrease where as the %s-character found to increase, moving from benzene to benzene...F–H and T-shaped benzene dimer. The van der Waal distance of separation is found to be 2.385 Å for benzene...F–H and 2.317 Å for T-shaped benzene dimer. The computed distance between the centers of mass of the two moieties in T-shaped benzene dimer is approximately 5 Å, which is in excellent agreement with the result from the microwave spectroscopy [32]. The natural charges at C-atom associated with the C–H bond is obtained as more negative and those at H-atom obtained as more positive in both benzene...F–H and T-shaped benzene dimer. However, it is worthy to be noticed that the \( \sigma_{C–H}^\parallel \) population \( (n(\sigma_{X–H}^\parallel)) \) of benzene has not changed in benzene...F–H. Recalling that Hobza and Havlas [12,13] have also pointed out that the electron density transfer from H-bond acceptor to remote highly electronegative atoms instead of \( \sigma_{X–H}^\perp \). It has also been suggested that unlike red-shifted H-bond, hyperconjugative \( n(Y) \rightarrow \sigma^*(X–H) \) is observed in the blue-shifted H-bond. The BSSE corrected binding energy is obtained as 1.035 kcal/mol for benzene...F–H and 1.864 kcal/mol for T-shaped benzene dimer (2.12 kcal/mol using MP2/6-311G** [28] and 1.95 kcal/mol using MP2/6-31+G//MP2/6-31G [33]).
Fig. 1a illustrates the correlation of C–H bond length with H⋯F distance in benzene⋯F–H system. It has been noted that different tendency are observed with different intermolecular distance with constraints. When the H⋯F distance has been kept fixed, the C–H bond lengths decrease with reducing intermolecular distance. Whereas by keeping the C⋯F bond length fixed, the C–H bond length found to be maximum for the H⋯F distance ranging from 3.1 to 3.3 Å. The C–H bond length increases with reducing H⋯F bond length from 5.0 to 3.3 Å and again it decreases with reducing H⋯F bond length from 3.1 to 2.4 Å. We have also examined the correlation of H⋯F distance with %sp-character of C–H bond (Fig. 1b) and with natural charges at C-atom and at H-atom of C–H (Fig. 1c), but no remarkable difference have been observed in those correlations.

Fig. 2 depicts the electrostatic contribution for the benzene⋯F–H system. It can be seen that when the H⋯F distance is being kept fixed (Fig. 2a), the attraction due to dipole-induced dipole interaction between H–F and remote part of benzene compresses the C–H bond. Consequently, reducing intermolecular distance, the attraction becomes larger; as a result the C–H bond is found to decrease. On the contrary, when the C⋯F distance is being kept fixed (Fig. 2b), the C–H bond length elongates due to the attraction between the positive H and the negative F. Accordingly, the electrostatic contributions for a general blue-shifted hydrogen bond system (Fig. 2c) can be realized as the attraction between remote part of H-bond donor and H-bond acceptor which is balanced by the repulsion between X–H bond and H-bond acceptor at equilibrium geometry.

In terms of electrostatic contributions, the σX⋯H bond may reach the potential minimum prior to the residual part of H-bond donor, as it is in the front of molecule. Then the remote part pushes the σX⋯H bond within the van der Waals separation between σX⋯H and H-bond acceptor. Therefore, the four-electron-two-orbital interaction between σX⋯H orbital and occupied orbitals of H-bond acceptor, such as lone pair and π orbital, should be observed in molecular orbital analysis. Moreover, if the effect of repulsive four-electron-two-orbital interaction on C–H bond overpowered the effect of two-electron-two-orbital interaction involving σX⋯H anti-bonding, the X⋯H bond would be shortened.

We have employed molecular orbital analysis for the T-shaped benzene dimer, which possess high symmetry. At MP2/6-311G (2d,p) level, the highest seven occupied orbitals of benzene are πe_1g, πe_2g, πa_2u, and πe_1u, and the lowest three unoccupied orbitals are πe_2u and πa_1g. During the formation of T-shaped benzene dimer, one of the highest occupied σ orbitals (e_2g) and the lowest unoccupied σ* orbital (a_1g) of the edge-to-face benzene

Table 1
Optimized geometry parameters and NBO analysis of improper H-bond complexes at MP2/6-311G (2d,p) level: (a) benzene; (b) benzene⋯F–H; (c) T-shaped benzene dimer

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<tr>
<th>Parameter</th>
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<th>Dhh (Å)</th>
<th>C2v (Å)</th>
<th>C2h (Å)</th>
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<td>r(C–H) (Å)</td>
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<td>Δr(C–H) (Å)</td>
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<td>–0.196</td>
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<td>n(σ_{C-H}) (electron)</td>
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<tr>
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<td>ΔE (kcal/mol)</td>
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<td>BSSE (kcal/mol)</td>
<td>D_{6h}</td>
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(EFB) turn to the $A_1$ representation, whereas those $\pi$ orbitals of the face-to-edge benzene (FEB), only the $a_{2u}$ orbital turns to the $A_1$ representation. Hence, two-orbital interactions can be expected, because of same symmetry: one between the $\pi a_{2u,FEB}$ and the $\sigma a_{1g,C3}$; the other between the $\pi a_{2u,FEB}$ and one of the $\sigma e_{2g,EFB}$. However, only the latter has been observed and shown in Fig. 3.

The energy difference between $\pi a_{2u}$ and $\sigma a_{1g}$ is found to be 0.65200 eV which is too large to form effective orbital interaction, though the $\pi a_{2u,FEB}$ is favorable to interact with the $\sigma a_{1g,EFB}$ in terms of symmetry. In contrast, the energy difference between $\pi a_{2u,FEB}$ and $\sigma e_{2g,EFB}$ is found to be only 0.00599 eV, which favors...
both for the orbital interaction and overlap as well. As a result, the orbital $2a_1 \left( \pi a_{2u, \text{FEB}} + \sigma c_{2g, \text{EFB}} \right)$ and $3a_1 \left( \pi a_{1u, \text{FEB}} / C_0 \right)$ are observed. Besides, we have also observed the orbital interaction between the $\pi a_{1u, \text{FEB}}$ and $\sigma c_{1u, \text{EFB}}$ to form $1a_1$ orbital in T-shaped benzene dimer along with the energy difference of about 0.08655 eV (see Fig. 3).

We have also examined the orbital interactions in benzene...F–H system, shown in Fig. 4. In terms of orbital symmetry, the lowest $\pi c_{1u}$ of benzene is found to be favorable to interact with the highest $\sigma$ of H–F contrary to the high energy difference value, 0.90824 eV. Further, it has been observed that the $\pi c_{1u}$ population $\langle n(\pi c_{1u}) \rangle$ of benzene in benzene...F–H has not increased as compared to benzene monomer.

4. Conclusion

The blue-shifted hydrogen bond is a result of the compression caused by two opposite types of interactions. One type is the attraction between H-bond acceptor and remote part of H-bond donor and the other type is the repulsion between X–H and H-bond acceptor. The results obtained from molecular orbital interactions reveal that there are orbital interactions between the $\pi c_{1u}$ orbitals of benzene and the occupied orbitals of the H-bond acceptors, whereas, the lowest $\sigma c_{1u}$ orbital of benzene is found unsuitable to accept electron, with respect to large orbital energy difference. We conclude that the repulsive four-electron-two-orbital interactions between the $\sigma c_{1u}$ orbitals of H-bond donor and the occupied orbitals of H-bond acceptor play an important role in the X–H bond shortening of blue-shifted hydrogen bond.

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References