

Electron density, interaction energy and hydrogen-bond radius of C–H...O interaction

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Atoms in theoretical analysis of molecules was used to study C–H...O interaction taking five different molecules with the same acceptor, O of water. The relation between electron density at hydrogen-bond critical point and interaction energy has been studied and hydrogen-bond radii were derived. Although a linear relationship was obtained like other intermolecular interactions, the value of linear parameters was found to be different when a similar type of interaction was compared suggesting that the parameters depend on the type of acceptor and donor and not the type of interaction. The H-bond radii for this type of interaction were found to have significant variance.

Keywords: Electron density, hydrogen-bond radius, interaction energy, linear parameters.

THE article by Sutor¹ in *Nature* is perhaps the first one regarding C–H...O hydrogen bond. Two decades after the article was published, Taylor, Kennard and Allen proved the existence of C–H...O hydrogen bond^{2,3}. Allen *et al.*² surveyed 113 published neutron diffraction crystal structures using the Cambridge Structural Database and proved the existence of not only C–H...O hydrogen bond, but also C–H...N and C–H...Cl hydrogen bond³. C–H...O hydrogen bond is now well established^{4,5}.

Several methods have been applied to detect hydrogen bonds. Some of them are spectroscopic techniques, diffraction data, quantum chemical calculations, etc. Although the first two methods have been in use from the very beginning to analyse hydrogen bonding, quantum chemical calculations have become popular now⁶.

Quantum theory of atoms in molecules (QTAIM or AIM) is another technique widely used nowadays for analysing hydrogen-bonding systems. Using this technique the topology of the electron density (ρ) of molecules, molecular complexes (clusters) or solids can be analysed⁷. The topology of the electron density contains important chemical and physical information^{7,8}. At certain points in the electron density map of a molecule, molecular complex or solid, the gradient of electron density ($\nabla\rho$) vanishes. These are called critical points and there are only four topologically stable critical points. Among these, bond critical points (BCPs) are important to characterize chemical bonding. The critical points are generally

labelled with the rank of Hessian of electron density and the sum of the sign of the eigenvalues of the Hessian (signature). For example, BCP has rank 3 (all critical points have rank 3) and signature -1 , and it can be labelled as (3, -1) critical point. This means at BCP (signature = -1) there are two negative eigenvalues along the transverse direction and one positive eigenvalue along the bond direction⁷.

According to Bader⁷, BCP along the bond path of the interacting atoms is the necessary and sufficient condition for two atoms to be bonded. This is applicable for all systems. However, for hydrogen-bonding, Koch and Popelier⁹ pointed out eight different criteria, including the presence of BCP. They considered five different diverse complexes (formaldehyde–chloroform, acetone–chloroform, benzene–formaldehyde, 1,1-dichloroethane–acetone and azidothymidine (commonly called AZT)) and characterized C–H...O hydrogen bonding on the basis of charge density.

Many other parameters are used to characterize hydrogen-bonding interactions. One of these is the distance between the donor and acceptor atoms. Several studies have pointed out that this distance should be less than the sum of van der Waals radii of the respective donor and acceptor atoms⁶. However, the inadequacy of this criterion has been documented in several studies, which have recommended the use of hydrogen-bond radii instead of van der Waals radii.

In the present study we have chosen C–H donor of five different molecules (methane, chloromethane, fluoromethane, malononitrile and pyridine) and same acceptor atom, O of water. All these donors have been well-studied and their bond dissociation energy, bond length, pKa, etc. are known^{14–18}. Further, there could be other types of hydrogen-bonding structures (for example, O–H...C bonding in CH₄...H₂O complex, O–H...F bonding in CH₃F...H₂O complex) for these complexes. Details about some of these complexes are available in the literature^{19,20}. As the primary aim in this study is to address the following two questions, we have optimized only C–H...O interactions. (i) Will there be a linear relationship between electron density at BCPs and interaction energy when the same donors from different molecules and the same acceptor are taken in C–H...O hydrogen bond? If so, will there be the same linear parameters compared to similar type of earlier study⁹? (ii) Hydrogen-bond radii have been defined for various donors and acceptors. What will be the variation of hydrogen-bond radii for C–H...O, when the same donors from different molecules and the same acceptor are taken?

The geometries of the molecules and complexes have been fully optimized at the MP2/6-311++G(d, p) level and frequency calculation at that level has also been carried out to ensure that true minima have been located as evidenced by the lack of imaginary frequencies. GAUSSIAN03 package was used to perform all electronic

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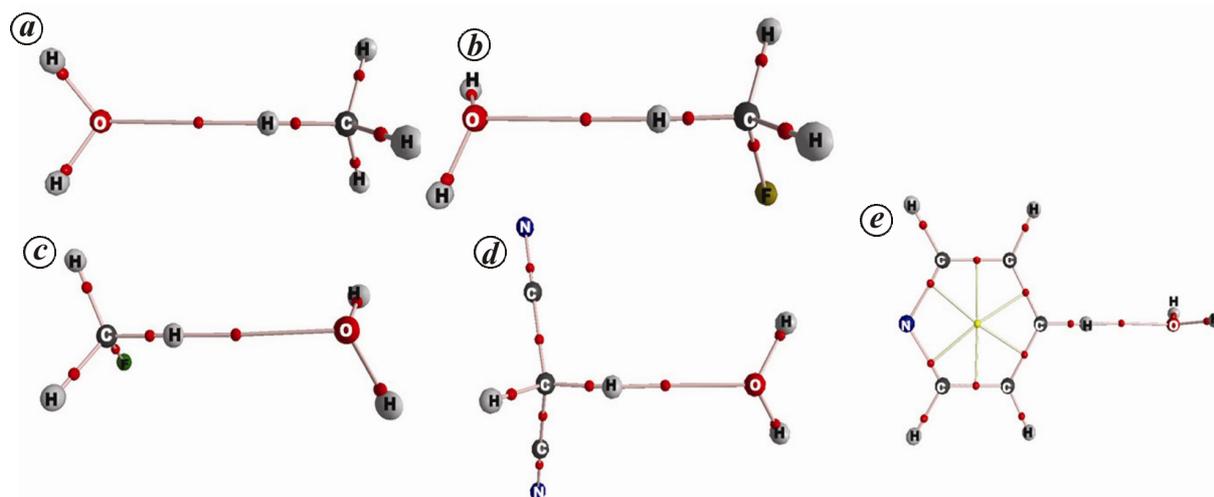


Figure 1. Molecular graph of five different complexes: *a*, methane–water complex; *b*, fluoromethane–water complex; *c*, chloromethane–water complex; *d*, malononitrile–water complex; *e*, pyridine–water complex.

Table 1. Interaction energy (ΔE , kJ/mol), electron density (ρ) and its Laplacian ($\nabla^2\rho$; in atomic units) of C–H...O and X–H...C (X = F, OH,) hydrogen bonding

Complex	ΔE	ρ	$\nabla^2\rho$
CH ₄ ...H ₂ O	-1.15 (-4.2)*, -6.3*	0.0078 (0.00723)*, 0.0079*	0.025 (0.027)*, 0.0331*
CH ₃ F...H ₂ O	-5.62, -16.50**	0.01, 0.0183**	0.0329, 0.0800**
CH ₃ Cl...H ₂ O	-6.58	0.0118	0.0387
(C=N) ₂ CH ₂ ...H ₂ O***	-18.8	0.0173	0.0625
Pyd...H ₂ O****	-7.26	0.0112	0.0393
Koch and Popelier ⁹ range for ρ and $\nabla^2\rho$		0.002–0.034	0.024–0.139

*Raghavendra and Arunan¹⁹; **Pyd Pyridine; *** $(C=N)_2CH_2$ is malononitrile; ****Rosenberg²⁰.

structure calculations²¹. Molecular graphs and electron density as well as its Laplacian were obtained using AIM2000 package²² with MP2/6-311++G** wave functions.

As mentioned earlier, we considered five different C–H...O complexes in this study. Figure 1 *a–e* shows the molecular graph of these complexes. All the complexes show covalent BCPs as well as BCP along the bond path of H atom and O atom. This is a validation of the existence of C–H...O hydrogen bonding. The BCPs in between H...O have been analysed in terms of electron density (ρ) and its Laplacian ($\nabla^2\rho$; Table 1). The values of H-bonded ρ are found to be in the range 0.0078–0.0112 atomic units (au). The values of $\nabla^2\rho$ are all positive and vary from 0.025 to 0.0625 au, thus showing the typical closed-shell interactions in these complexes. These values of ρ and $\nabla^2\rho$ are well within the range given by Koch and Popelier⁹ (Table 1).

It is possible that there could be other structures for the complexes studied in this work. For example, CH₄...H₂O complex was studied by Raghavendra and Arunan¹⁹ and it may be worthwhile to compare our results with theirs (see Table 1). The data within parenthesis and asterisk in Table 1 are for C–H...O interaction and those with aster-

isk only are for O–H...C interaction. It can be seen from Table 1 that the values obtained for interaction energy is much lower than those of Raghavendra and Arunan¹⁹. This may be due to the basis set. Raghavendra and Arunan used aug-cc-pvtz basis set, while we have used 6-311++G(d, p) basis set. However, we do not have definite answer on this because there is not much more variation in the values of ρ and $\nabla^2\rho$. Table 1 also shows that the values of interaction energies are found to be higher for O–H...C interaction compared to C–H...O interaction. Therefore, O–H...C bonding structure may be the minimum structure in comparison to C–H...O bonding structure.

Rosenberg²⁰ studied the hydrogen bonding structure of CH₃F...H₂O complex and optimized O–H...F hydrogen bonding interaction. We have provided these data²⁰ in Table 1. Like the CH₄...H₂O complex, O–H...F hydrogen bonding structure is found to be more stable when compared with data of Rosenberg²⁰.

The BSSE-corrected interaction energy is also given in Table 1. The interaction energy is higher for malononitrile–water complex and lower for methane–water complex. Boys–Bernardi²³ counterpoise procedure was used for BSSE correction. A linear relationship was found between the interaction energy values and the

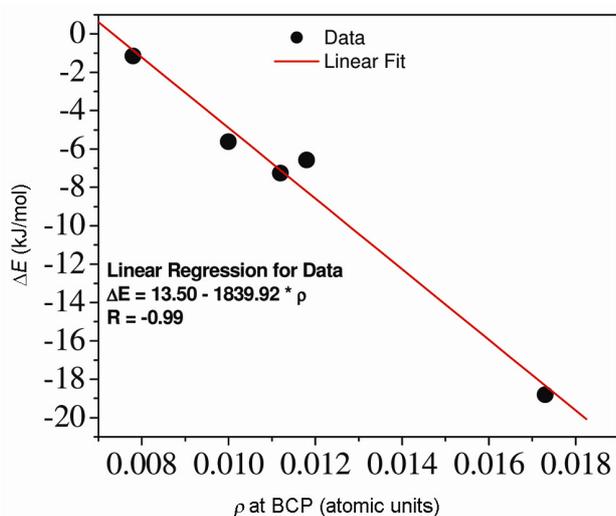
Table 2. Linear parameters for different types of interactions (ΔE in kJ/mol, ρ in atomic units)

Type of interaction	Linear parameters (slope and intercept)
Our data, C–H...O interaction	$\Delta E = 13.50 - 1840 * \rho$
Koch and Popelier ⁹ , C–H...O interaction	$\Delta E = 1.59 - 996 * \rho$
Raghavendra and Arunan ²⁴ , H-, Li-, and Cl-bonding interactions	$\Delta E = 5.1 - 1100 * \rho$ (for H-bonding) $\Delta E = 8.9 - 1161 * \rho$ (for Cl-bonding) $\Delta E = 13.1 - 3215 * \rho$ (for Li bonding)
Shahi and Arunan ²⁵ , H-, Li-, and Cl- bonding interactions	$\Delta E = 0.4 - 777 * \rho$ (for H-bonding) $\Delta E = 0.3 - 776 * \rho$ (for Cl-bonding) $\Delta E = 17.6 - 3271 * \rho$ (for Li bonding)
Parajuli and Arunan ²⁶ , Na-bonding interactions	$\Delta E = 18.0 - 4694 * \rho$ (for all acceptors studied in ref. 26) $\Delta E = 13.4 - 3428 * \rho$ (for acceptors as in ref. 24)

Table 3. R_{H-BCP} (H-bonded radius; Å) and R_{A-BCP} (distance between acceptor to H-bond critical point (acceptor radius; Å)) from atoms in molecules (AIM) theoretical analysis

Complex	R_{H-BCP}	R_{A-BCP}
CH ₄ ...H ₂ O	1.01	1.53
CH ₃ F...H ₂ O	0.94	1.47
CH ₃ Cl...H ₂ O	0.9	1.44
(C=N) ₂ CH ₂ ...H ₂ O*	0.8	1.33
Pyd...H ₂ O**	0.91	1.42
Average***	0.91 ± 0.08	1.44 ± 0.07
Raghavendra <i>et al.</i> ¹¹	1, 0	1, 4

*(C=N)₂CH₂, Malononitrile; **Pyd, Pyridine; ***Error is standard deviation.

**Figure 2.** Plot of interaction energy as a function of electron density at the H-bonding critical point.

corresponding electron densities at H-bonded BCP (Figure 2), leading the following equation with excellent correlations ($R = -0.99$)

$$\Delta E = 13.50 - 1840 \times \rho,$$

where ΔE is in kJ/mol and ρ in atomic units.

Similar kinds of linear relationship were found in other types of interaction as well^{24–26}. Table 2 presents the linear parameters of different interactions.

Now the question may arise: are the linear parameters the same when compared with similar types of interaction? Arunan and co-workers^{24,25} studied Li-bonded, Cl-bonded and H-bonded systems and found that the slopes of Cl-bonded and H-bonded systems were similar when the same acceptors were taken, and different for Li-bonded system. This can be clearly seen from Table 2. Moreover, it can be seen from Table 2 that Na-bonded and Li-bonded systems have similar slopes^{24,26}. As mentioned earlier, we have also obtained a linear relationship between interaction energy and electron density at H-bonded BCPs in this study, but we have obtained different linear parameters (both slope and intercept) compared to Koch and Popelier⁹ ($\Delta E = 1.59 - 996 * \rho$; Table 2). This result suggests that the linear parameters depend on the type of acceptor and donor and not on the type of interaction in the case of hydrogen bonding. It should be noted that in some of the studies^{24,26}, interaction energies are in kcal/mol and we have converted these values to kJ/mol (Table 2).

Hydrogen-bond radii have been derived from AIM analysis^{11–13} and following the same procedure Li-bond radii and Na-bond radii were also determined²⁶. Similarly, hydrogen-bond radii for C–H...O interaction were derived by calculating the distance between hydrogen atom and BCP (R_{H-BCP}), while acceptor radii were derived by calculating the distance between acceptor atom and BCP (R_{A-BCP}). Table 3 shows these results. It can be seen that there is variation of hydrogen-bond radius for all the five complexes. The hydrogen-bond radius of malononitrile–water complex is found to be smaller and that of methane–water complex is found to be large. This is because of the C–H donor; the C–H donor of malononitrile is more acidic in comparison to other molecules, and the C–H donor of methane is less acidic¹⁸. Similar results were also reported in earlier studies¹¹. It has been well-established that H-bond radii^{10–13} and Cl-bond radii²⁷ have significant variance; however, Na-bond radii and Li-bond radii¹⁹ have a much smaller variance. The same

trend was observed for C–H···O hydrogen bond similar to other H-bonding systems (Table 3).

We compared our data for hydrogen-bond radii with those of other studies^{10–13}. Arunan *et al.*¹¹ estimated C–H hydrogen-bond radius from the C–H dipole moment of HCCH. According to their approximation, C–H hydrogen-bond radius was 1.0 Å (Table 3). Using this value they calculated C=O distance of formaldehyde, and this distance was considered as the acceptor radius (1.4 Å) for the C–H donor (Table 3). These values (both hydrogen-bond radius and acceptor radius) are comparable with our data.

Based on electron density topology, Klein¹³ calculated H-bond radius of various types of hydrogen-bonding interactions. He estimated C–H···O interaction distance to be 1.5 Å using 0.002 au electron density counter. This was the van der Waal's radius of O atom for the C–H···O interaction. Moreover, acceptor radius (average value = 1.44 Å in our calculation) should not be more than this distance, indicating that both results are in good agreement.

C–H···O hydrogen bond has been analysed taking five different molecules for C–H donor and O of water as acceptor in terms of electron density at H-bonded BCP, interaction energy and hydrogen-bond radius. Similar to other earlier studies, we found a linear relationship in this type of interaction. However, we obtained different linear parameters when a similar type of interaction was compared. The hydrogen-bond radii for C–H···O interaction were also found to have significant variance like other H-bonded interactions.

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