

# Competition between halogen, dihalogen and hydrogen bonds in bromo- and iodomethanol dimers

Kevin E. Riley · Jan Řezáč · Pavel Hobza

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**Abstract** O-H...X and O-H...O H-bonds as well as C-X...X dihalogen and C-X...O halogen bonds have been investigated in halomethanol dimers (bromomethanol dimer, iodomethanol dimer, difluorobromomethanol...bromomethanol complex and difluoroiodomethanol...iodomethanol complex). Structures of all complexes were optimized at the counterpoise-corrected MP2/cc-pVTZ level and single-point energies were calculated at the CCSD(T)/aug-cc-pVTZ level. Energy decomposition for the bromomethanol dimer complex was performed using the DFT-SAPT method based on the aug-cc-pVTZ basis set. OH...O and OH...X H-bonds are systematically the strongest in all complexes investigated, with the former being the strongest bond. Halogen and dihalogen bonds, being of comparable strength, are weaker than both H-bonds but are still significant. The strongest bonds were found in the difluoroiodomethanol...iodomethanol complex, where the O-H...O H-bond exceeds 7 kcal mol<sup>-1</sup>, and the halogen and dihalogen bonds exceed 2.5 and 2.3 kcal mol<sup>-1</sup>, respectively. Electrostatic energy is dominant for H-bonded structures, in halogen bonded structures

electrostatic and dispersion energies are comparable, and, finally, for dihalogen structures the dispersion energy is clearly dominant.

**Keywords** Dihalogen bond · Halogen bond · Hydrogen bond · Noncovalent interactions

## Introduction

A RX...YZ halogen bond is an attractive interaction where X is a halogen (usually Cl, Br or I) that is a part of the RX molecule and YZ is a Lewis base; Y is often an atom having a lone electron pair (e.g., O, N, S) [1, 2]. Because X and Y are electronegative atoms which are typically negatively charged, the existence of the halogen bond is counterintuitive. It has, however, been shown that the electrostatic potential around a halogen covalently bound to an electronegative (or roughly electroneutral) atom, such as carbon, possesses a region of positive charge on the extension of covalent RX bond, which is called the  $\sigma$ -hole. The remainder of the halogen generally has a negative potential [3–5]. A halogen bond thus occurs between a positively charged  $\sigma$ -hole and negatively charged atom Y. Y can also be a halogen, with the resulting interaction termed a dihalogen bond [1, 6, 7]. In this case bonding is realized between a positively charged  $\sigma$ -hole and negatively charged remainder of another halogen. When X is H then we have a classical RH...YZ H-bond and in this case Y could be O, N, S or a halogen. Since the  $\sigma$ -hole is generally rather small, the R-X...Z motif in halogen and dihalogen bonds should be almost linear, with the linearity of halogen and dihalogen bonds being higher than that of the corresponding H-bond. The same argument holds for the orthogonality of the R-X and Y-Z bonds in a dihalogen bonds. H-bonds are the strongest among all noncovalent interactions and highly accurate binding energies (in kcal mol<sup>-1</sup>) can be found in the

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Dedicated to the 75th birthday of our distinguished colleague and friend, Peter Politzer

K. E. Riley (✉)  
Department of Chemistry, Xavier University of Louisiana,  
New Orleans, LA 70225, USA  
e-mail: kev.e.riley@gmail.com

J. Řezáč · P. Hobza  
Institute of Organic Chemistry and Biochemistry, Academy of  
Sciences of the Czech Republic, 166 10 Prague, Czech Republic

P. Hobza  
Regional Center of Advanced Technologies and Materials,  
Department of Physical Chemistry, Palacky University,  
771 46 Olomouc, Czech Republic

recently published S66 dataset: [8] O-H...O (water dimer and methanol dimer) 4.9 and 5.8, N-H...N (methylamine dimer) 4.2, N-H...O (methylamine...methanol) 3.1 and C-H...O (acetylene...water) 2.9. Halogen bonded complexes are weaker but they are generally thought to be stronger than complexes with dihalogen bonds. These comparisons can be ambiguous, since in practically all cases different complexes are being compared. Halomethanol dimers represent complexes where all three mentioned intermolecular bonds (halogen, dihalogen and two different H-bonds) co-exist. By varying the halogen atom it is possible to modify the strength of all these bonds. The strengths of all these interactions can also be modified by replacement of hydrogens by fluorines. In this case the  $\sigma$ -hole on the halogen atom becomes more positive, which results in stronger binding [9]. Fluorine substitution can also modify a molecule's electronic distribution such to produce a stronger positive charge on the -OH hydrogen, producing stronger hydrogen bonds [10].

The aim of the present paper is to investigate the properties of various noncovalent interactions occurring in dimers of halomethanol dimers. To the best of our knowledge, no similar study comparing the different intermolecular bonds that co-exist within one complex have been carried out. Specifically, the C-X...O halogen bond, C-X...X dihalogen bond, as well as O-H...O and O-H...X hydrogen bonds will be investigated in the bromomethanol and iodomethanol dimers. One particular interest we have in this study is the effect of fluorine substitution on the halogen bond or hydrogen bond donor. The substitution of these electronegative atoms can have a major impact on the size and charge of a halogen's  $\sigma$ -hole and, thus, can influence the strength of a halogen bonding interaction. Thus we also investigate the difluorobromomethanol...bromomethanol and difluoroiodomethanol...iodomethanol complexes in order to compare these interactions with those of the unsubstituted dimers.

To obtain reliable interaction energies it is necessary to perform high-level calculations and the CCSD(T) method, when combined with an extended basis set, represents a suitable tool [11]. The CCSD(T) method provides accurate total interaction energies, but for understanding the differences between various intermolecular bonds it would be profitable to decompose total interaction energies into its component parts. The symmetry-adapted perturbation theory (SAPT) [12] and, more specifically, its DFT version (DFT-SAPT) [13] provide reliable energy components that are physically well defined.

## Computations

The geometries of isolated subsystems and the respective complexes were optimized at the counterpoise-corrected MP2/cc-pVTZ level. We have shown [14] that complex

geometries determined at this level are close to those calculated at the CCSD(T)/extended basis set level. Fluorine substitutions have been made to the bond donors (i.e., hydrogen bond donor, halogen bond donor, or dihalogen bond donor) of both parent complexes considered here (i.e.,  $\text{H}_2\text{CBrOH}\dots\text{H}_2\text{CBrOH} \rightarrow \text{F}_2\text{CBrOH}\dots\text{H}_2\text{CBrOH}$ ). The structures of these, fluorine substituted, complexes were then reoptimized. Single-point energies were evaluated at the CCSD(T)/aug-cc-pVTZ level, which again has been demonstrated [10] to produce very accurate binding energies. For all CCSD(T) calculations, the halogens (either Br or I) are described using the aug-cc-pVTZ-PP basis set, which includes pseudopotentials that implicitly describe relativistic effects.

The DFT-SAPT interaction energy is given by Eq. 1.

$$E(\text{int}) = E(\text{elec}) + E(\text{ind}) + E(\text{disp}) + E(\text{exch}) + \delta(\text{HF}) \quad (1)$$

The terms in Eq. 1 refer to electrostatic, induction, dispersion, exchange-repulsion and higher-order terms. The second and third energies include their corresponding exchange parts (i.e.,  $E(\text{disp})$  includes dispersion-exchange contributions). The last term covers the higher-order Hartree-Fock contributions (mainly due to induction and charge-transfer). The DFT-SAPT calculations were performed using the aug-cc-pVTZ basis set, which should result in reasonably consistent values for all decomposition terms, with the possible exception of dispersion, which might be underestimated by roughly 5 %, as shown by Řezáč et al. [15].

In order to visualize the distribution of charges in the bromomethanol and difluorobromomethanol molecules, electrostatic potentials have been generated for these molecules. These electrostatic potentials have been computed on the molecular "surfaces," taking this to be an outer contour of the electronic density on the 0.001 au (electrons/bohr<sup>3</sup>) surface, as proposed by Bader et al. [16]. Here electrostatic potentials were computed at the B3LYP/6-31+G\*\* level of theory using the WFA program [17].

All geometry optimizations, CCSD(T) binding energies, and DFT-SAPT interaction decompositions were carried out using Molpro 2010 [18].

## Results

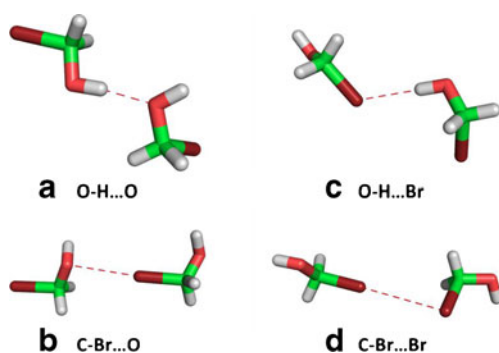
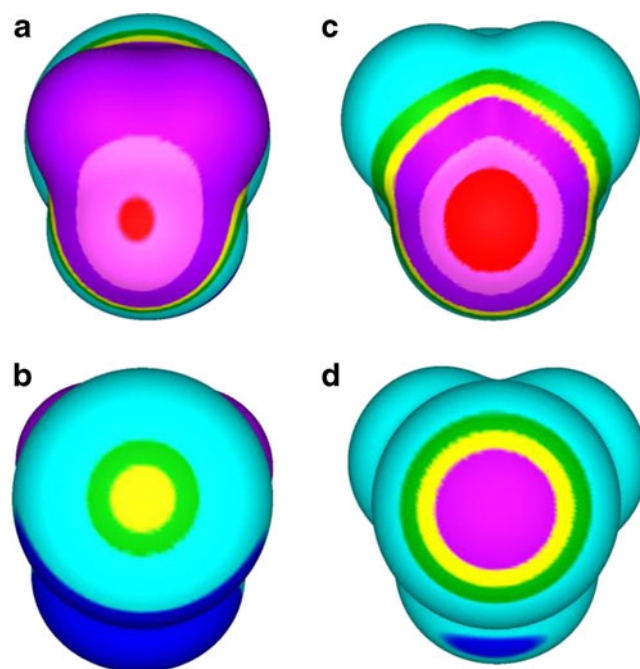
Geometries of all subsystems and respective complexes are presented in Table 1. Structures of all four types of bromomethanol dimer are visualized in Fig. 1 (structures of all complexes presented in this work are available in supplementary material, Figs. S1 and S2). Investigating these structures for the bromomethanol dimer we find the closest contacts (in Å) for the OH...O H-bond (H...O 1.89) followed by the OH...Br

**Table 1** Bond distances (in Å) and bond angles (parentetical, in degrees) for all interactions considered in this work

	O-H...X	O-H...O	C-X...X	C-X...O
H <sub>2</sub> CBrOH... H <sub>2</sub> CBrOH	2.57 (175.7)	1.89 (169.8)	3.81 (173.0)	3.12 (175.2)
F <sub>2</sub> CBrOH... H <sub>2</sub> CBrOH	2.41 (175.4)	1.77 (170.3)	3.66 (176.4)	3.05 (178.1)
H <sub>2</sub> CIOH... H <sub>2</sub> CIOH	2.70 (151.9)	1.85 (170.8)	3.93 (174.6)	3.30 (171.6)
F <sub>2</sub> CIOH... H <sub>2</sub> CIOH	2.58 (169.6)	1.73 (171.3)	3.76 (177.7)	3.13 (174.5)

H-bond (2.57), CBr...O halogen bond (3.12) and CBr...Br dihalogen bond (3.81). All these distances are shorter than the sum of the relevant van der Waals radii, which are given as supplementary material in Table S3. The expected linearity of the halogen and dihalogen bonds are fulfilled ( $\angle$  C-Br...O = 175°,  $\angle$  C-Br...Br = 174°) and the same is true for the orthogonality of the Br...Br-C (90.0°) motif in the dihalogen bond. The linearity of the O-H...Br H-bond (176°) is, as expected, higher than that of the O-H...O H-bond (170°). The geometric data for the remaining three complexes are all very similar to those discussed for the bromomethanol dimer, with one significant exception. In the iodomethanol dimer, the O-H...I hydrogen bond angle diverges from linearity significantly ( $\angle$  O-H...I = 151.9). The most likely explanation for the deviation of this angle from linearity is the presence in the optimized structure of a second interaction that occurs between the two iodines in the complex.

Figure 2 shows electrostatic potentials for the bromines and OH groups in the bromomethanol and difluorobromomethanol molecules. Here it can be seen that the replacement of the two methyl hydrogens with fluorines results in a larger  $\sigma$ -hole on bromine and a more positively charged –OH hydrogen. It is thus expected that fluorine substitution in the hydrogen and halogen bond donor molecules

**Fig. 1** Optimized structures of O-H...Br and O-H...O H-bonded structures, C-Br...Br dihalogen bonded and C-Br...O halogen bonded structure of the bromomethanol dimer. H...Br, H...O, Br...Br and Br...O distances as well as O-H...Br, O-H...O, C-Br...Br and C-Br...O angles are given in Table 1. In the case of the dihalogen bond (C-Br...Br), the Br...Br-C angle is 90.0°**Fig. 2** Electrostatic potentials showing (a) the OH side of bromomethanol, (b) the Br side of bromomethanol, (c) the OH side of difluorobromomethanol, and (d) the Br side of difluorobromomethanol. The color ranges are as follows (in kcal mol<sup>-1</sup>): red, greater than 55; light purple, from 35 to 55; dark purple, from 10 to 35; yellow, from 5 to 10; yellow, from 0 to 5; light blue, from -15 to 0; dark blue, less than -15

should lead to stronger interactions with stronger electrostatic character.

Table 2 shows the CCSD(T)/aug-cc-pVTZ interaction energies for the H-bonded (O-H...X and O-H...O), dihalogen-bonded (C-X...X) and halogen-bonded (C-X...O) forms of all complexes studied. The strongest bond in all these complexes is the O-H...O H-bond, followed by the O-H...X H-bond, the halogen bond (C-X...O) is the third strongest and the dihalogen bond (C-X...X) is the weakest, but the differences between the halogen and dihalogen bonds are small. Passing from Br to I all bonds with the exception of the O-H...O H-bond become stronger by between 30 and 50 % and, as

**Table 2** CCSD(T)/aug-cc-pVTZ interaction energies (in kcal mol<sup>-1</sup>) for H-bonded (O-H...X and O-H...O), dihalogen-bonded (C-X...X) and halogen-bonded (C-X...O) forms of complexes investigated (X=Br, I). Numbers in parentheses refer to relative strength (compared to strongest H-bond) of different complex forms

	O-H...X	O-H...O	C-X...X	C-X...O
H <sub>2</sub> CBrOH... H <sub>2</sub> CBrOH	-2.98 (58)	-5.10 (100)	-1.22 (24)	-1.48 (29)
F <sub>2</sub> CBrOH... H <sub>2</sub> CBrOH	-4.53 (66)	-6.91 (100)	-1.73 (25)	-1.91 (28)
H <sub>2</sub> CIOH... H <sub>2</sub> CIOH	-3.87 (75)	-5.18 (100)	-1.77 (34)	-1.98 (38)
F <sub>2</sub> CIOH... H <sub>2</sub> CIOH	-4.37 (62)	-7.03 (100)	-2.33 (33)	-2.59 (37)

expected, roughly the same enhancement of stability for all bonds (including the O-H...O H-bond) results upon substituting fluorines for hydrogens in the bond donor. In comparison with the O-H...O H-bond, the halogen and dihalogen bonds in the bromomethanol dimer and difluorobromomethanol...bromomethanol complex are relatively weak (25 and 29 %, respectively). These interactions are stronger (in terms of both relative and absolute values) for the iodomethanol dimer and difluoroiodomethanol...iodomethanol complex (34 and 38 %, respectively). All bonds become strongest in the difluoroiodomethanol...iodomethanol complex, where H-bonds, halogen and dihalogen bonds, exceed 7.0 (O-H...O), 4.3 (O-H...X), 2.5 (C-X...O) and 2.3 (C-X...X) kcal mol<sup>-1</sup>. In relative numbers this is 100 % : 62 % : 37 % : 33 % (respectively). We can thus conclude that though these halogen and dihalogen bonds are weaker than strong H-bonds they are still relatively strong and their strength is comparable to that of weaker H-bonds (see above). Halogen and dihalogen bonds can thus play an important role in stabilizing intermolecular species.

Table 3 shows DFT-SAPT interaction energies as well as their components for the bromomethanol dimer. DFT-SAPT and CCSD(T) interaction energies were determined with the same basis set (although DFT-SAPT calculations did not utilize the pseudopotential-containing aug-cc-pVTZ-PP basis sets on halogens). The DFT-SAPT stabilization energies are systematically larger than the CCSD(T) ones and this difference is largest for H-bonded and dihalogen bonded structures (12 and 8 %, respectively), which both have the bromine atom as an electron donor. We do not have any explanation for this result and expected to receive similar interaction energies, as is true in the case of the other two forms that have the oxygen atom as the electron donor. It is possible that the absence of pseudopotentials on bromine in our DFT-SAPT computations is responsible (or partially responsible) for the discrepancy between CCSD(T) and DFT-SAPT.

The energy decomposition clearly demonstrates that, in the case of the H-bonded systems, the electrostatic term is dominant, while for halogen and dihalogen structures the

dispersion energy plays the largest role in stabilization. This finding is in agreement with the results of Riley et al., who show that the dispersion interaction plays a dominant role in C-X...O halogen bonds involving small  $\sigma$ -holes, while electrostatics played a larger role in substituted systems with larger  $\sigma$ -holes [19]. In the case of the halogen bonded structure, the electrostatic and dispersion terms are comparable, while dispersion is clearly dominant in the case of the dihalogen bonded complex. The energy of the dihalogen bond is roughly comparable to that of the halogen bond, and from energy decomposition it is evident that this is due to the dispersion contribution, which is dominant here. This is not surprising since in these complexes two highly polarizable atoms (two halogens) are close together, which makes the respective dispersion energy contribution substantial. Induction effects, which are described by the E(ind) term as well as the  $\delta$ (HF) term (whose main contributions come from higher-order induction), play a smaller role in all four types of interactions than electrostatics and dispersion. Making the approximation that the total induction contribution for a given interaction is the sum of the E(ind) and  $\delta$ (HF) terms, it is seen that induction plays a larger role in the hydrogen bonding complexes than in the halogen bonding and dihalogen complex. Among the four interaction types investigated here, induction makes its largest contribution in the O-H...X hydrogen bond (E(ind)+ $\delta$ (HF)=-2.99 kcal mol<sup>-1</sup>) and its smallest contribution for the (C-X...X) dihalogen bond (E(ind)+ $\delta$ (HF)=-0.31 kcal mol<sup>-1</sup>).

## Conclusions

The main conclusions that can be drawn from our studies on complexes of halomethanols and difluoromethanols are that, for these complexes:

- i OH...O and OH...X H-bonds are systematically the strongest in all complexes investigated and the former one is always the strongest bond.
- ii Halogen and dihalogen bonds, which are comparably strong to each other, are weaker than both H-bonds but they are still relatively strong.
- iii The strongest bonds were found for the difluoroiodomethanol dimer, where the O-H...O H-bond exceeds 7 kcal mol<sup>-1</sup> and the halogen and dihalogen bonds exceed 2.5 and 2.3 kcal mol<sup>-1</sup>, respectively.
- iv The linearity of halogen and dihalogen bonds is higher than that of H-bonds.
- v The electrostatic energy is dominant for H-bonded structures while the dispersion energy plays the largest role in stabilization for halogen and, especially, dihalogen structures (although electrostatics are still important for these interactions).

**Table 3** Interaction energy components (in kcal mol<sup>-1</sup>) for bromomethanol dimer evaluated at the DFT-SAPT/aug-cc-pVTZ level; second-order dispersion and induction energies include their exchange components

	O-H...X	O-H...O	C-X...X	C-X...O
E(elec)	-2.99	-7.52	-0.98	-2.48
E(exch)	4.28	9.00	1.94	4.30
E(ind)	-1.12	-1.86	-0.13	-0.21
E(dis)	-2.92	-3.66	-2.09	-2.88
$\delta$ (HF)	-0.60	-1.13	-0.18	-0.29
E(int)	-3.33	-5.16	-1.44	-1.55

It should be noted here that all of the interaction types studied here can vary greatly depending on their chemical environment. For example, halogen bonds with binding energies exceeding  $-5.0 \text{ kcal mol}^{-1}$  have been observed in some studies [8].

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## References

1. Metrangolo, P, Resnati G (eds.) (2008) Halogen bonding with dihalogens and interhalogens, in halogen bonding. In: Fundamentals and applications. Springer, Berlin, p 126
2. Politzer P, Lane P, Concha MC, Ma Y, Murray JSJ (2007) *Mol Model* 13:305–311
3. Brinck T, Murray JS, Politzer P (1992) *Int J Quant Chem Quant Biol Symp* 19:57–64
4. Politzer P, Murray JS, Concha MCJ (2007) *Mol Model* 13:643–650
5. Auffinger P, Hays FA, Westhof E, Ho PS (2004) *Proc Natl Acad Sci U S A* 101:16789–16794
6. Awwadi F, Willett RD, Twamley B (2011) *Cryst Growth Des* 11:5316–5323
7. Politzer P, Murray JS, Concha MCJ (2008) *Mol Model* 14:659–665
8. Rezac J, Riley KE, Hobza PJ (2011) *Chem Theory Comput* 7:2427–2438
9. Riley KE, Murray JS, Politzer P, Concha MC, Hobza PJ (2009) *Chem Theory Comput* 5:155–163
10. Riley KE (2009) *Int J Quant Chem* 110:1833–1841
11. Riley KE, Pitonak M, Jurecka P, Hobza P (2010) *Chem Rev* 110:5023–5063
12. Jeziorski B, Moszynski R, Szalewicz K (1994) *Chem Rev* 94:1887–1930
13. Jansen G, Hesselmann AJ (2001) *Phys Chem A* 105:11156–11157
14. Dabkowska I, Jurecka P, Hobza PJ (2005) *Chem Phys* 122:204322
15. Řezáč J, Hobza PJ (2011) *Chem Theory Comput* 7:685–689
16. Bader RFW, Carroll MT, Cheeseman JR, Chang CJ (1987) *Am Chem Soc* 109:7968–7979
17. Bulat FA, Toro-Labbe A, Brinck T, Murray JS, Politzer PJ (2010) *Mol Model* 16:1679–1691
18. Werner HJ, Knowles PJ, Lindh R, Manby FR, Sch€utz M, Celani P, Korona T, Rauhut G, Amos RD, Bernhardsson A, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer, G, Lloyd AW, McNicholas SJ, Meyer W, Mura ME, Nicklaß A, Palmieri P, Pitzer P, Schumann U, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T (2008) MOLPRO, version 2010.1
19. Riley KE, Murray JS, Fanfrlik J, Rezac J, Sola RJ, Concha MC, Ramos FM, Politzer PJ (2012) *Mol Model* doi:10.1007/s00894-012-1428-x