Science in China Series B: Chemistry

© 2008 SCIENCE IN CHINA PRESS
Springer

www.scichina.com
chem.scichina.com
www.springerlink.com

Theoretical study of bifurcated bent blue-shifted hydrogen bonds $CH_2\cdots Y$

LI AnYong

School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China (email: aylifnsy@swu.edu.cn)

Ab initio **quantum chemistry methods were applied to study the bifurcated bent hydrogen bonds Y⋯H_2CZ (Z = O, S, Se) and Y⋯H_2CZ_2 (Z = F, Cl, Br) (Y = Cl^-, Br^-) at the MP2/6-311++G(d,p) and MP2/6-311++G(2df,2p) levels. The results show that in each complex there are two equivalent blue-shifted H-bonds Y⋯H—C, and that the interaction energies and blue shifts are large, the energy of each Y⋯H—C H-bond is 15—27 kJ/mol, and Δr(CH) = –0.1 — –0.5 pm and $\Delta \nu$(CH) = 30 — 80 cm^{-1}. The natural bond orbital analysis shows that these blue-shifted H-bonds are caused by three factors: large rehybridization; small direct intermolecular hyperconjugation and larger indirect intermolecular hyperconjugation; large decrease of intramolecular hyperconjugation. The topological analysis of electron density shows that in each complex there are three intermolecular critical points: there is one bond critical point between the acceptor atom Y and each hydrogen, and there is a ring critical point inside the tetragon YHCH, so these interactions are exactly H-bonding.**

bifurcated bent H-bonds, blue-shifted H-bonds, topological property of electron density, intramolecular hyperconjugation

1 Introduction

Hydrogen bonding is very important in chemistry and biochemical processes[1—3]. The classical H-bond usually takes place between an acid (proton donor) XH bond and a base Y (proton acceptor), here X and Y are electronegative atoms such as O, N, F or Cl, and Y has lone pairs of electrons or π electrons. The classical H-bonds, named red-shifted H-bonds, are characteristic of elongation of the XH bond and decrease of the XH stretch frequency and increase of the IR intensity. In recent years, it is found that the C—H, Si—H, N—H and P—H bonds and so on can act as the proton donors to form essentially different H-bonds from the classical H-bonds, which, called blue-shifted H-bonds, are characteristic of contraction of the XH bond and decrease of the XH stretch frequency, and also exist extensively in chemical and biological systems. The blue-shifted H-bonds are more complicate than the red- shifted, whose physical and chemical essences are still studied. Currently, two theories are proposed to interpret the blue-shifted H-bonds Y⋯H—XZ. Hobza[4] proposed a two-step mechanism that firstly, electron density is transferred from n(Y) to σ*(XZ), then the structure of the proton donor reorganizes, and consequently the HX bond contracts and its vibrational frequency is blue-shifting. Alabugin and Weinhold[5] proposed that all H-bonds including red- and blue-shifted H-bonds could be interpreted by use of the concepts of hyperconjugation and rehybridization. Hyperconjugation transfers electron density from n(Y) to σ*(XH) and leads to red- shifted H-bonds; rehybridization is a shortening effect on the XH bond accompanying repolarization of the XH bond under electrostatic field of the proton acceptor and increase of the s-character of X hybrid of the XH bond. Balance of hyperconjugation and rehybridization determines red shift or blue shift of the formed H-bond. In

Received August 14, 2007; accepted November 23, 2007
doi: 10.1007/s11426-008-0064-x

my previous work[6], I found that intramolecular hyperconjugation between the remote lone pair n(Z) and σ*(XH) in the proton donor HXZ, which was not considered by Alabugin, is also an important factor which can adjust electron density on σ*(XH) and determine red- and blue- shift of the H-bonds together with intermolecular hyperconjugation n(Y)→ σ*(XH) and rehybridization. Moreover, the theory of Hobza is a special case of the theory of intra- and intermolecular hyperconjugations and rehybridization.

The usual H-bonds are monofurcated and linear interactions between one proton acceptor Y and one donor HX, the H-bonding angle is usually more than 120°. In crystal structures and biological systems, there are multifurcated H-bonds between one acceptor Y and several donors HX[7], the H-bonding angle is usually smaller than 110°, and their properties are usually different from those of linear H-bonds. In my previous work[8], we found that the bifurcated H-bonds OC(CO)⋯H_2NF are blue- shifted, the acceptor atom C(O) is equal-distant from the two hydrogen atoms, the H-bonding angle is small, about 90°, and that the intermolecular hyperconjugation n(O,C) → σ*(NH) and rehybridization of N in σ(NH) are very small and can be neglected. In this case, the theory of hyperconjugation and rehybridization of Alabugin cannot be used, but the theory of Hobza is successful in explaining blue shifts of these H-bonds. So, we conjecture that the multi-furcated bent H-bonds are mostly blue-shifted, and their electronic properties have essential differences from those of the usual monofurcated linear H-bonds. For answering this problem, we studied a great number of multifurcated H-bonds. In this article, we report a type of bifurcated H-bonds Y⋯H_2CZ(Z = O, S, Se) and Y⋯H_2CZ_2 (Z= F, Cl, Br)(Y= Cl^-, Br^-), analyze their frequency shifts, topological properties of electron density and interaction between natural bond orbitals (NBOs), and interpret their formation using current theories, and compare them with the usual linear H-bonds.

2 Computation methods

In this article we use the Gaussian 03 programs[9] to optimize the geometrical structures of the monomers and complexes and perform frequency calculations at the MP2/6-311++G(d,p) and MP2/6-311++G(2df,2p) levels. The interaction energies are computed with correction of the basis set superposition error (BSSE) and without corrections of the zero-point vibrational energies (ZPE). The BSSE corrections of interaction energies were computed using the function counterpoise procedure proposed by Boys and Bernardi[10]: $\delta_{AB}^{BSSE} = E_{AB}^{A}(A) + E_{AB}^{B}(B) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B)$, where $E_{Y}^{X}(Z)$ represents the energy of system Z at the geometry Y with the basis set X.

The topological properties of electron density for the monomers and complexes were computed at the MP2/6-311++G(d,p) level by use of the theory of atoms in molecules (AIM)[11] and AIM2000 programs[12−14]. The properties at the critical points and the integration properties in the hydrogen atomic basin are obtained. In addition, the NBO analysis for all the monomers and complexes was performed at the MP2/6-311++G(d,p) level using the GenNBO5.0 Programs[15], we obtained the interaction characters between the NBOs. These results of the NBO analysis are important for exploring the essences of H-bonds.

3 Results and discussions

3.1 Geometrical structures, vibrational frequencies and interaction energies

The optimized complexes have symmetry of C_{2v} at the two theoretical levels, the anions Cl^- and Br^- are equal-distant from the two hydrogen atoms. In Figure 1 we show the geometrical structures of the complexes, the bond lengths of the donors, the Y⋯H distance (nm) and the H-bonding angles ∠YHC(°) at the level of MP2/6-311++G(d,p). The H-bonding angles are in the range 104°—108°, largely smaller than those (>120°) of the monofurcated H-bonds, so these bifurcated H-bonds are very bent, which will influence many electronic properties of the formed H-bonds.

In these complexes, the four Y⋯H_2CO and Y⋯H_2CF_2 systems have no imaginary frequency and so are minima in the potential energy surfaces (PESs); but all other complexes optimized at the two levels have one imaginary frequency (16i — 74i cm^{-1}), and so are saddles in the PESs. The imaginary vibrational mode implies that the monofurcated H-bond is stable for these systems, and our calculation on the corresponding monofurcated H-bonds confirmed this conclusion. We also optimized the bifurcated and monofurcated H-bonds between F^- and H_2CZ (Z = O, S, Se), H_2CZ_2 (Z = F, Cl, Br) at the MP2/6-311++G(d,p) level, and found each of

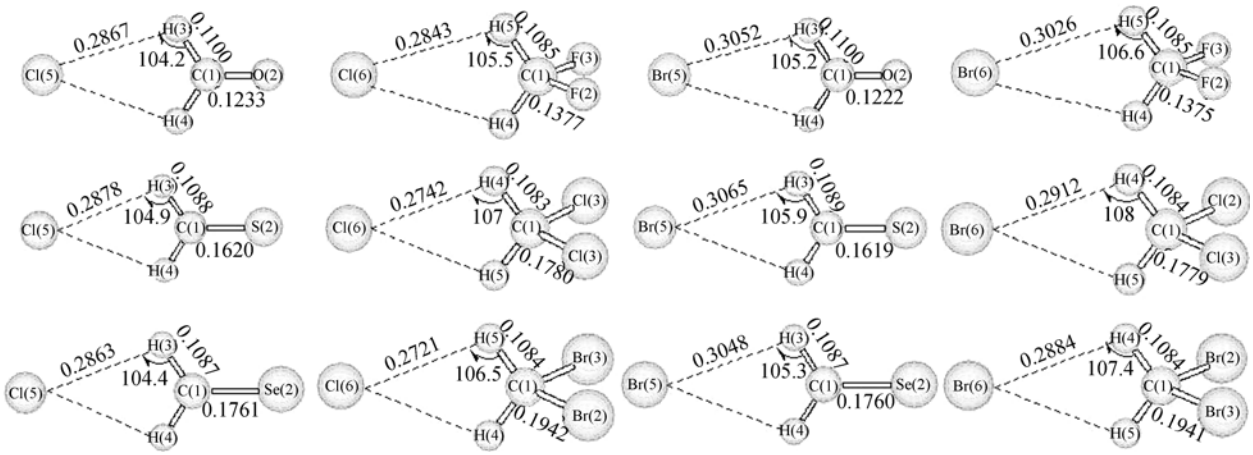

Figure 1 Geometry of the Cl^- and Br^- complexes (MP2/6-311++G(d,p)).

the bifurcated H-bonds has one imaginary frequency (111i — 215i cm^{-1}, $F^- \cdots H_2CS$ has one more small imaginary frequency), and the monofurcated H-bonds are minima in the PESs. In addition, we also optimized the bifurcated H-bonds between I^- and H_2CZ (Z = O, S, Se), H_2CZ_2 (Z = F, Cl, Br) at the MP2/3-21G level, and obtained the same results as Cl^- and Br^-, that is, $I^- \cdots H_2CO$ and $I^- \cdots H_2CF_2$ are stable, whose geometrical structures are shown in Figure 2, but the other systems are saddles. We also recalculated the complexes of F^-, Cl^- and Br^- at the MP2/3-21G level, and obtained the same results with the two large basis sets (except for $Br^- \cdots H_2CF_2$ which has one small imaginary frequency), so the results of the I^- systems at the MP2/3-21G level are reasonable. Overall, our calculated results show that among the bifurcated H-bonds between F^-, Cl^-, Br^- and I^- and H_2CZ_n, only the minority of the acceptors Cl^-, Br^- and I^- with the donors of Z = O and F are stable, the others are saddles.

We suppose that the stability of these bifurcated H-bonds is mainly determined by the size of Y, that is, diffusibility of electron cloud, and electronegativity of the Z atom. The larger Y, the more diffuse its electron cloud, the easier Y forms bifurcated H-bonds with the two hydrogen atoms; the larger the electronegativity of Z, the more negative the Z′s charge in H_2CZ_n, then exclusion between Z and Y inhibits formation of monobifurcated H-bonds, and is of advantage for formation of bifurcated H-bonds. From the AIM calculation at the MP2/3-21G level we obtain the anion radii of F^-, Cl^-, Br^- and I^- (equal to the distance from the nuclear to the 0.001 a.u. electron density contour): 2.85, 4.13, 4.27 and 4.79 a.u., the last three are close and much larger than the first, so it is the small radius of F^- such that it can not form stable bifurcated H-bonds with H_2CZ_n. The NBO analysis at the MP2/6-311++G(d,p) level shows that in the donors H_2CO and H_2CF_2, carbon has a positive charge (0.397, 0.619 e, respectively), O and F have negative charges (–0.580, –0.416 e, respectively); in H_2CCl_2, carbon has a large negative charge (–0.310 e), Cl has a small negative charge (–0.035 e); in H_2CS, H_2CSe and H_2CBr_2, carbon has a large negative charge (–0.355, –0.440, –0.494 e, respectively), S, Se and Br have small positive charges (0.023, 0.097, 0.046 e, respectively). So in the complexes of Cl^-, Br^- and I^-, it is the different electronegativity of the Z atom such that the donors with Z = O and F can, but those with Z = S, Se, Cl and Br cannot, form stable bifurcated H-bonds.

Table 1 lists the changes of the CH and CZ bond

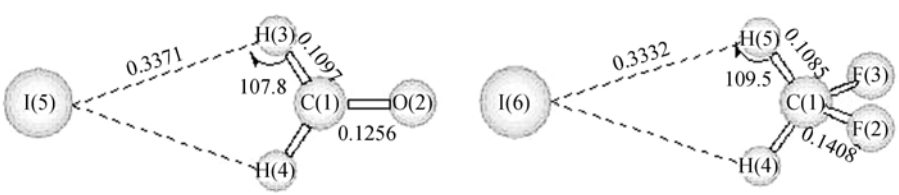

Figure 2 Geometry of the stable I^- complexes (MP2/3-21G).

Table 1 Changes of the CH and CZ bond lengths (nm) and their vibrational frequencies (cm^{-1}), interaction energies E_{int} and BSSE ($kJ \cdot mol^{-1}$)

Properties	$Cl^-\cdots H_2CO$	$Cl^-\cdots H_2CS$	$Cl^-\cdots H_2CSe$	$Br^-\cdots H_2CO$	$Br^-\cdots H_2CS$	$Br^-\cdots H_2CSe$	$Cl^-\cdots H_2CF_2$	$Cl^-\cdots H_2CCl_2$	$Cl^-\cdots H_2CBr_2$	$Br^-\cdots H_2CF_2$	$Br^-\cdots H_2CCl_2$	$Br^-\cdots H_2CBr_2$
Δr(CH)	–0.0005	–0.0003	–0.0002	–0.0005	–0.0002	–0.0002	–0.0005	–0.0003	–0.0002	–0.0005	–0.0003	–0.0002
Δr(CZ)	0.0010	0.0006	0.0004	0.0009	0.0005	0.0004	0.0017	0.0013	0.0013	0.0015	0.0012	0.0011
$\Delta \nu$(CH)	62,86	44,48	38,39	53,77	38,43	33,34	63,80	46,48	36,39	54,69	39,43	31,34
$\Delta \nu$(CZ)	–23	–8	2	–20	–7	2	–44,–66	–27,–37	–18,–29	–39,–58	–25,–33	–17,–26
E_{int}	–41.54	–34.74	–35.13	–38.09	–31.71	–32.06	–44.90	–45.84	–47.29	–40.85	–41.89	–43.45
BSSE	7.14	7.77	7.74	5.91	6.56	6.43	8.13	11.61	11.10	6.83	10.19	9.49
Δr(CH)[a)]	–0.0004	–0.0002	–0.0001	–0.0004	–0.0002	–0.0001	–0.0005	–0.0002	–0.0001	–0.0004	–0.0002	–0.0001
$\Delta \nu$(CH)[a)]	54,77	38,41	32,31	46,69	32,37	27,28	56,76	35,35	–	49,68	–	–
E_{int}[a)]	–46.28	–41.69	–40.35	–42.18	–37.86	–36.57	–47.30	–52.33	–54.40	–42.71	–47.46	–49.57
BSSE[a)]	4.78	5.49	5.36	2.67	3.31	3.16	5.51	6.93	7.15	3.23	4.34	4.47

a) Represent the results at the MP2/6-311++G(2df,2p) level. Other values are the results at the MP2/6-311++G(d,p) level. Z = O, S, Se, F, Cl, Br

lengths, their stretch frequencies, the interaction energies and the BSSE corrections for the Cl^- and Br^- complexes. All these bifurcated H-bonds are blue-shifted at the two levels of theory, the blue shifts are large, Δr(CH) = –0.1 —–0.5 pm, $\Delta \nu$(CH) = 30 — 80 cm^{-1}. In addition, the CZ bond elongates and its stretch frequency decreases (except for the Se-systems) on complexation. Red shift of the CZ bond interprets blue shift of the CH bond and supports the theory of Hobza. Moreover, for the same proton acceptor, both blue shift of the CH bond and red shift of the CZ bond decrease in the order Z = O, S and Se, or F, Cl and Br of the donor, so the changes of the CH bond are correlated with changes of the CZ bond, which again supports Hobza' theory.

The interaction energies of these H-bonds are large, being 30—54 kJ/mol with the BSSE correction; the energy of each H-bond is 15—27 kJ/mol, much larger than the energy (~10 kJ/mol) of the linear blue-shifted H-bond, and also a little larger than that of the usual red-shifted H-bond (10—20 kJ/mol)[16]. For the bifurcated H-bonds $Y\cdots H_2C{=}Z$ of the same acceptor, the interaction energies decrease in the order Z = O, S and Se; but for the bifurcated H-bonds $Y\cdots H_2CZ_2$ of the same acceptor, the interaction energies increase in the order Z = F, Cl and Br. This rule is more explicit for the results with the large basis set. So for the two types of H-bonds, the correlation of the energy with frequency shift is positive for one type but negative for the other, which shows that the blue-shifted H-bonds are complex.

The bifurcated H-bonds between I^- and H_2CZ (Z = O, S, Se), H_2CZ_2 (Z= F, Cl, Br) at the MP2/3-21G level are also blue-shifted, Δr(CH) = –0.1— –0.4 pm, $\Delta \nu$(CH) = 20—65 cm^{-1}, and the CZ bond is red-shifted. The interaction energies with BSSE correction are 18 — 42 kJ/mol.

3.2 Topological properties of electron density

The theory of atoms in molecules (AIM) proposed by Bader, which analyzes topological properties of electron density, is a powerful tool of studying chemical bonds, intermolecular interactions and H-bonds. As Bader pointed out[11], the interatomic interactions have mainly two classes: (a) the shared interactions which mainly exist in covalent bonds, at the bond critical point (BCP, (3, –1) critical point) $\rho(r_c)$ is large (>0.1 a.u.) and $\nabla^2\rho(r_c)$ is negative, and the three non-zero eigenvalues $\lambda_1 \leqslant \lambda_2 < 0 < \lambda_3$ of the Hessian matrix of $\rho(r_c)$ satisfy $|\lambda_1|/\lambda_3 > 1$; (b) the closed-shell interactions found in ionic bonds, hydrogen bonds and van der Waals molecules, at the BCP $\rho(r_c)$ is small (< 0.1 a.u.) and $\nabla^2\rho(r_c)$ is positive, and $|\lambda_1|/\lambda_3 < 1$.

Bader[11] investigated some typical H-bonds and deduced the basic characteristics of topological properties of electron density for a H-bond that in the H-bonding complexes, the hydrogen atom in question is bonded to the acid fragment (part of the proton donor) by a shared interaction and to the base (the proton acceptor) by a closed-shell interaction. This description can be used as a definition of the H-bonds. Popelier[17] studied the Y⋯HC H-bonds and proposed eight criteria for existence of H-bonds: (i) correct topological pattern: the existence of a BCP and bond paths and interatomic surface between Y and H; (ii) proper value of electron density at this BCP: 0.002—0.034 a.u.; (iii) proper value of Laplacian of electron density at this BCP: 0.024—0.139 a.u.; (iv)

mutual penetration of H and Y atoms; (v) increase of hydrogen net charge; (vi) energetic destabilization of hydrogen; (vii) decrease of dipolar polarization of the hydrogen atom; (viii) decrease of hydrogen atomic volume. This definition is cumbersome and too reliant on calculated characteristics to be of practical use, as pointed out by Hobza. Comparatively, the definition of Bader may be more practical.

The usual monofurcated linear H-bonds satisfy the definition of Bader, and the properties at the intermolecular BCP and the integration properties in the hydrogen atomic basin also satisfy most of the criteria of Popelier. The multifurcated H-bond is very bent and the Y⋯HX angle is small, which generally leads to the topological properties of electron density very different from those of the linear H-bonds. For exploring this problem, we performed topological analysis of electron density for the systems in this article at the MP2/6-311++G(d,p) level.

The calculated results show that for each of the systems, there are three intermolecular critical points (ICPs): one BCP between the acceptor Y and each hydrogen atom, and one ring critical point (RCP, (3,+1) critical point) inside the tetragon YHCH, as shown in Figure 3. In Figure 3, we plot gradient paths of electron density at the symmetry plane containing the H atoms for the Cl^- complexes, those of the Br^- complexes are similar and neglected. Here the bold lines represent the special gra-

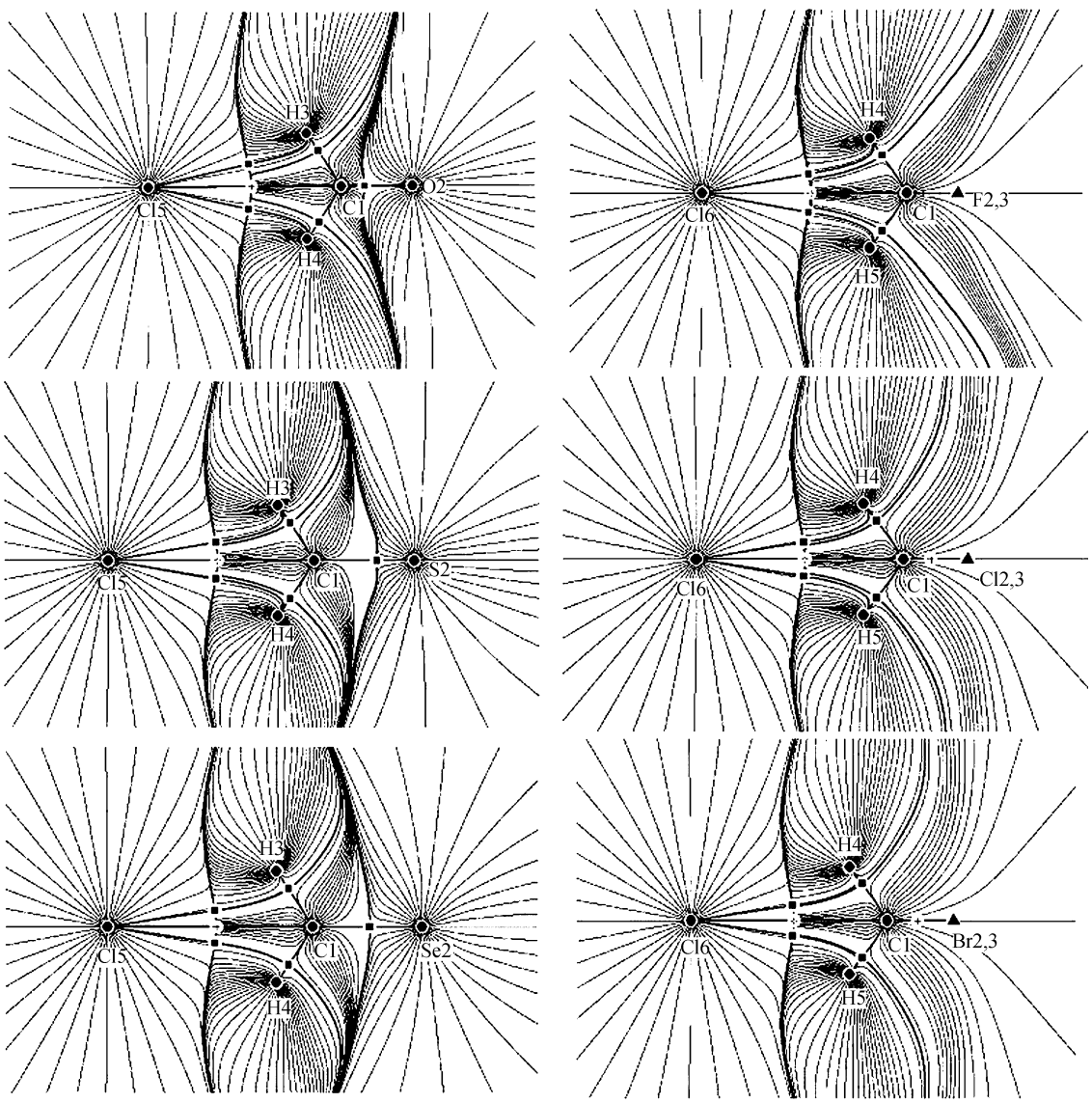

Figure 3 Gradient paths of electron density for the complexes of the acceptor Cl^-.

dient paths; the circles and triangles represent the (3, –3) critical points (nuclei) in and out of the plotting plane, respectively; the rectangles and crosses represent the BCPs in and out of the plotting plane, respectively; and the ring critical point is represented by a crosslight. Table 2 lists the properties at the intermolecular BCPs and RCPs, which show that the critical point between Y and H is indeed a BCP and the interaction between Y and H is closed-shell interaction. All these systems satisfy the definition of Bader, and also satisfy the first criterion of Popelier's definition, so these interactions are similar to the usual linear H-bonds and can be exactly classified as H-bonds.

We consider the other criteria of Popelier for these H-bonds. The values in Table 2 show that electron density and Laplacian at all the intermolecular BCPs and RCPs are in the ranges proposed by Popelier. Table 3 lists the integration properties in the H atomic basin, which show that on complexation, the net charge and atomic energy of hydrogen increase, the atomic volume of hydrogen decreases, the sum of radii of H and Y decreases ($\Delta r_H + \Delta r_Y < 0$, $\Delta r = r - r_0$, where the bonded radius r in complexes is defined as the distance from a nucleus to the BCP in question, and the nonbonded radius r_0 in monomers is defined as the distance of a nucleus to the 0.001 a.u. electron density contour). So these systems satisfy the criteria 4, 5, 6 and 8 of Popelier. However, the atomic dipolar moment of hydrogen increases for all but three systems, not consistent with Popelier's criterion 7. Totally, these bifurcated interactions almost satisfy all of Popelier's criteria, and can be exactly classified as H-bonding.

Table 3 also lists the changes of electron density at the BCPs of the HC and CZ (Z = O, S, Se, F, Cl, Br) bonds in the proton donors. We found that on complexation, ρ_c(HC) increases, and ρ_c(CZ) decreases (except that in the S and Se systems ρ_c(CZ) has a small but negligible increment). Since electron density at the BCP is correlated with strength of a covalent bond, increase of ρ_c(HC) and decrease of ρ_c(CZ) are respectively consistent with blue shift of the HC bond and red shift of the CZ bond on formation of the H-bonds. On the other hand, strength of a covalent bond is correlated with its bond order, and so with the occupancies in the bonding and antibonding orbitals; since the occupancy in bonding orbitals almost does not change on formation of a

Table 2 Properties (a.u.) at the intermolecular BCPs and RCPs: eigenvalues λ_1, λ_2 and λ_3 of the Hessian matrix of $\rho(r_c)$, electron density $\rho(r_c)$, Laplacian $\nabla^2\rho(r_c)$ of electron density and $|\lambda_1|/\lambda_3$

Systems	ICP	λ_1	λ_2	λ_3	ρ_c	$\nabla^2\rho_c$	$\lvert\lambda_1\rvert/\lambda_3$
$Cl^-\cdots H_2CO$	(3, –1)	–0.00647	–0.00332	0.04315	0.00877	0.03337	0.14985
	(3,+1)	–0.00614	0.00254	0.04099	0.00848	0.03738	0.14987
$Cl^-\cdots H_2CS$	(3, –1)	–0.00621	–0.00199	0.04195	0.00869	0.03375	0.14796
	(3,+1)	–0.00605	0.00127	0.04086	0.00860	0.03607	0.14805
$Cl^-\cdots H_2CSe$	(3, –1)	–0.00659	–0.00173	0.04416	0.00914	0.03584	0.14931
	(3,+1)	–0.00647	0.00105	0.04324	0.00908	0.03782	0.14962
$Cl^-\cdots H_2CF_2$	(3, –1)	–0.00696	–0.00240	0.04540	0.00912	0.03603	0.15342
	(3,+1)	–0.00685	0.00157	0.04408	0.00899	0.03881	0.15530
$Cl^-\cdots H_2CCl_2$	(3, –1)	–0.00868	–0.00223	0.05459	0.01109	0.04368	0.15897
	(3,+1)	–0.00854	0.00135	0.05306	0.01101	0.04588	0.16087
$Cl^-\cdots H_2CBr_2$	(3, –1)	–0.00920	–0.00210	0.05738	0.01168	0.04609	0.16028
	(3,+1)	–0.00906	0.00124	0.05592	0.01161	0.04810	0.16203
$Br^-\cdots H_2CO$	(3, –1)	–0.00523	–0.00284	0.03450	0.00765	0.02643	0.15162
	(3,+1)	–0.00495	0.00223	0.03283	0.00736	0.03011	0.15074
Br^-+H_2CS	(3, –1)	–0.00503	–0.00177	0.03374	0.00761	0.02694	0.14907
	(3,+1)	–0.00488	0.00115	0.03285	0.00752	0.02913	0.14860
$Br^-\cdots H_2CSe$	(3, –1)	–0.00532	–0.00154	0.03530	0.00798	0.02845	0.15060
	(3,+1)	–0.00520	0.00095	0.03456	0.00792	0.03031	0.15053
$Br^-\cdots H_2CF_2$	(3, –1)	–0.00561	–0.00214	0.03631	0.00795	0.02855	0.15465
	(3,+1)	–0.00550	0.00144	0.03526	0.00782	0.03120	0.15602
$Br^-\cdots H_2CCl_2$	(3, –1)	–0.00714	–0.00209	0.04450	0.00985	0.03527	0.16041
	(3,+1)	–0.00700	0.00130	0.04328	0.00976	0.03757	0.16186
$Br^-\cdots H_2CBr_2$	(3, –1)	–0.00765	–0.00202	0.04732	0.01049	0.03765	0.16175
	(3,+1)	–0.00752	0.00122	0.04610	0.01042	0.03980	0.16319

Table 3 Integration properties in the H atomic basin and electron density at the BCPs of the HC and CZ bonds (a.u.)[a)]

Systems	$\Delta r_H+\Delta r_Y$	Δq_H	ΔE_H	$\Delta\lvert M_H\rvert$	ΔV_H	$\Delta\rho_c$(HC)	$\Delta\rho_c$(CZ)
$Cl^-\cdots H_2CO$	−1.17467	0.04489	0.01871	0.00560	−2.55003	0.00611	−0.01002
$Cl^-\cdots H_2CS$	−1.06130	0.06243	0.02601	−0.00105	−3.50779	0.00532	0.00024
$Cl^-\cdots H_2CSe$	−1.06358	–	–	–	–	0.00529	0.00051
$Cl^-\cdots H_2CF_2$	−1.10899	0.05344	0.02479	0.00625	−2.61237	0.00560	−0.01510
$Cl^-\cdots H_2CCl_2$	−1.25566	0.06740	0.03083	−0.00072	−4.15126	0.00430	−0.00850
$Cl^-\cdots H_2CBr_2$	−1.26551	0.07252	0.03408	0.00191	−3.83115	0.00402	−0.00485
$Br^-\cdots H_2CO$	−1.03215	0.04097	0.01846	0.00813	−1.70912	0.00550	−0.00907
$Br^-\cdots H_2CS$	−0.92596	0.05911	0.02581	0.00232	−2.69392	0.00486	0.00010
$Br^-\cdots H_2CSe$	−0.92587	0.05289	0.02103	−0.00772	−3.12620	0.00485	0.00048
$Br^-\cdots H_2CF_2$	−0.97540	0.05049	0.02472	0.00917	−1.97602	0.00497	−0.01353
$Br^-\cdots H_2CCl_2$	−1.15082	0.06139	0.02868	0.00103	−3.54474	0.00393	−0.00771
$Br^-\cdots H_2CBr_2$	−1.17478	0.06574	0.03141	0.00254	−3.37401	0.00369	−0.00434

a) ΔA = A(in complexes)−A (in monomers). *q*, atomic net charge of H; *E*: total atomic energy of H; *M*, dipole moment of H; *V*, volume of H

H-bond, so increase of ρ_c(HC) and decrease of ρ_c(CZ) imply decrease of occupancy in σ*(CH) and increase of occupancy in σ*(CZ), respectively. We deduce that electron density coming from the acceptor Y is transferred not to σ*(CH) but to σ*(CZ) of the donor. This conclusion will be clearer by use of the NBO analysis in the next subsection, the charge transfer analyzed by the AIM method may be coarse, more precise by the NBO method.

It is worthy of notation that in the trajectory maps of Figure 3, the path between hydrogen and the intermolecular BCP bends toward the inside of the tetragon YHCH, and approach successively to the path between the RCP and the CH bond's BCP as the Z atom of the donor H_2CZ_n (n =1, 2) varies from O(F) to Se(Br). For the Se and Br systems, these two paths almost fold; especially for $Cl^-\cdots H_2CSe$, the two paths can not be distinguished by the computer′s precision, which leads to the integration properties in hydrogen atomic basin much larger than those of the other systems and leads to wrong values, which are not listed in Table 3. In addition, in the systems $Y\cdots H_2C{=}Z$, the interatomic surfaces between C and Z changes from inward to outward.

We also performed AIM analysis for the bifurcated H-bonds $I^-\cdots H_2CZ$ (Z = O, S, Se) and $I^-\cdots H_2CZ_2$ (Z= F, Cl, Br) at the MP2/3-21G level, and found that the topological properties of electron density of the two stable complexes $I^-\cdots H_2CO$ and $I^-\cdots H_2CF_2$ have the same characters as those of the Cl^- and Br^- complexes, that is, there are three intermolecular critical points: one BCP between I^- and each hydrogen atom, and one RCP inside the tetragon IHCH; but the topological properties of electron density of the other complexes have distinct differences: there is only one BCP between I^- and carbon.

3.3 NBO analysis

For the purpose of exploring the origins of these bifurcated bent blue-shifted H-bonds, we performed NBO calculation for the monomers and complexes at the MP2/6-311++G(d,p) level. Tables 4 and 5 list the results for the systems $Y\cdots H_2C{=}Z$ (Z=O, S, Se) and $Y\cdots H_2CZ_2$ (Z = F, Cl, Br) (Y = Cl^-, Br^-), respectively, including electron density transfer (EDT) between monomers, hyperconjugation energies $E\{n \rightarrow \sigma^*\}$ between NBOs, variations of occupancies on the NBOs: Δn and Δσ*, variations Δs(C) and Δp(C) of the s character of C hybrid of the CH bond and polarization percentage of σ(CH) on C hybrid.

In all these systems there are relatively large electron density transfer from the acceptor Y to the donor such that the occupancy on n(Y) decreases, EDT ≈ −Δn(Y). The intermolecular hyperconjugation energy implies the acceptor-NBO of electron density transfer. For the $Y\cdots H_2C{=}Z$ systems, $E\{n(Y) \rightarrow \sigma^*(CH)\}$ is very small, but $E\{n(Y) \rightarrow \sigma^*(CZ)\}$ is much larger, which implies that the main part of electron density coming from Y is transferred to σ*(CZ), not to σ*(CH). For the $Y\cdots H_2CZ_2$ systems, as Z varies from F to Br, $E\{n(Y) \rightarrow \sigma^*(CH)\}$ changes from larger to smaller than $E\{n(Y) \rightarrow \sigma^*(CZ)\}$, their factor is from 2 to 1/2, their difference is not so large as in the $Y\cdots H_2C{=}Z$ systems, so the magnitudes of electron density transferred to σ*(CZ) and to σ*(CH) have no distinct difference. We call the hyperconjugation n(Y) → σ*(CH) direct intermolecular hyperconjugation, which transfers electron charge from

Table 4 NBO results of $Y\cdots H_2C{=}Z$ (Z = O, S, Se; Y = Cl^-, Br^-)[a)]

Properties	$Cl^-\cdots H_2CO$	$Cl^-\cdots H_2CS$	$Cl^-\cdots H_2CSe$	$Br^-\cdots H_2CO$	$Br^-\cdots H_2CS$	$Br^-\cdots H_2CSe$
EDT	0.00669	0.00861	0.01060	0.00685	0.00841	0.01032
$\Delta E\{n(Z)–\sigma^*(CH)\}$	–12.47	–8.28	–6.40	–11.30	–7.45	–5.65
$E\{n(Y)–\sigma^*(CH)\}$	1.76	0.67	0.63	1.76	0.84	0.50
$E\{n(Y)–\sigma^*(CZ)\}$	5.77	6.44	8.20	4.10	5.69	7.32
$\Delta\sigma^*(CH)$	–0.01106	–0.00808	–0.00588	–0.00984	–0.00734	–0.00526
$\Delta\sigma^*(CZ)$	0.00245	0.00389	0.00546	0.00242	0.00371	0.00526
$\Delta n(Z)$	0.01167	0.00942	0.00725	0.01064	0.00859	0.00654
$\Delta n(Y)$	–0.00721	–0.00881	–0.01072	–0.00727	–0.00860	–0.01044
Δs (%)	0.49	0.47	0.45	0.44	0.43	0.42
$\Delta p(C)$ (%)	1.23	1.23	1.17	1.12	1.11	1.05

a) $E\{n \rightarrow \sigma^*\}$: kJ /mol

Table 5 NBO results of $Y\cdots H_2CZ_2$ (Z = F, Cl, Br; Y = Cl^-, Br^-)[a)]

Properties	$Cl^-\cdots H_2CF_2$	$Cl^-\cdots H_2CCl_2$	$Cl^-\cdots H_2CBr_2$	$Br^-\cdots H_2CF_2$	$Br^-\cdots H_2CCl_2$	$Br^-\cdots H_2CBr_2$
EDT	0.00586	0.01075	0.01467	0.00594	0.01047	0.01464
$\Delta E\{n(Z)–\sigma^*(CH)\}$	–9.62	–8.37	–6.44	–8.70	–7.78	–5.94
$E\{n(Y)–\sigma^*(CH)\}$	2.47	2.13	2.01	2.68	2.18	2.01
$E\{n(Y)–\sigma^*(CZ)\}$	1.46	3.31	4.69	1.26	2.89	4.27
$\Delta E\{n(Z')–\sigma^*(CZ)\}$	–5.10	–2.51	–1.88	–4.73	–2.43	–1.72
$\Delta\sigma^*(CH)$	–0.00626	–0.00590	–0.00402	–0.00540	–0.00530	–0.00354
$\Delta\sigma^*(CZ)$	0.00056	0.00436	0.00866	0.00044	0.00406	0.00854
$\Delta n(Z)$	0.01454	0.01642	0.01362	0.01328	0.01526	0.01262
$\Delta n(Y)$	–0.00529	–0.01091	–0.01482	–0.00561	–0.01070	–0.01482
$\Delta s(C)$ (%)	0.95	1.23	1.36	0.84	1.13	1.27
$\Delta p(C)$ (%)	1.55	1.87	1.91	1.41	1.71	1.76

a) $E\{n \rightarrow \sigma^*\}$: kJ /mol

n(Y) to σ*(CH) and leads to red-shifted H-bonds; and we call the hyperconjugation n(Y) → σ*(CZ) indirect intermolecular hyperconjugation, which transfers electron charge from n(Y) to σ*(CZ) and leads to blue-shifted H-bonds according to Hobza′s theory. For the $Y\cdots H_2C{=}Z$ systems, indirect hyperconjguation is larger and has contribution to blue shifts of the formed H-bonds; for the $Y\cdots H_2CZ_2$ systems, direct and indirect hyperconjugations may cancel each other's effects on the formed H-bonds.

In the usual monofurcated H-bonds, the direct hyperconjugation is usually very large, and there is no indirect hyperconjugation. However, in these bifurcated H-bonds the direct interaction is small, but the indirect interaction is relatively large. The reason is that the monofurcated H-bond is usually linear or almost linear, but the bifurcated H-bond is very bent. In the bent configuration of bifurcated H-bonds, n(Y) and σ*(CH) have small or no overlap and weak interaction; conversely, n(Y) and σ*(CZ) may have larger overlap and stronger interaction.

For the same proton acceptor, EDT, –Δn(Y), Δσ*(CZ) and $E\{n(Y) \rightarrow \sigma^*(CH)\} + E\{n(Y) \rightarrow \sigma^*(CZ)\}$ increase according to the order Z = O, S and Se, or F, Cl and Br of the donor, they are positively correlated with each other. Especially, EDT is well linearly correlated with –Δn(Y), and the linear coefficient is close to 1. These properties have been discussed in my previous paper[6].

On formation of these H-bonds, the intramolecular hyperconjugation between n(Z) and σ*(CH) in the proton donor decreases, $\Delta E\{n(Z) \rightarrow \sigma^*(CH)\} < 0$, which causes a large magnitude of electron density on σ*(CH) flowing back to n(Z) such that occupancy on σ*(CH) largely decreases but occupancy on n(Z) largely increases, and ultimately, leads to the CH bond strengthening and shortening. So in these systems large decrease of intramolecular hyperconjugation has large contribution to blue shifts of the formed H-bonds. For the same proton acceptor, Δσ*(CH) and $\Delta E\{n(Z) \rightarrow \sigma^*(CH)\}$ decrease in the order Z = O, S and Se, or F, Cl and Br, they are positively correlated. For the systems $Y\cdots H_2CZ_2$ the hyperconjugation n(Z′) → σ*(CZ) in the donor decreases, especially for the F systems, which causes electron charge on σ*(CZ) flowing back to n(Z′)

such that occupancy on n(Z) largely increases. The same reason interprets that occupancy on σ*(CZ) has little increment for the F systems.

In all these bifurcated H-bonds, there is relatively large rehybridization, the *s* character of C hybrid of the CH bond and the polarization percentage of σ(CH) on C hybrid have large increments, especially for the Y⋯H_2CZ_2 systems, Δ*s*(C) is about 1%. According to the theory of Alabugin, large rehybridization has large contribution to blue shift of the H-bond.

We also performed NBO analysis for the bifurcated blue-shifted H-bonds I^-⋯H_2CZ (Z = O, S, Se) and I^-⋯H_2CZ_2 (Z= F, Cl, Br) at the MP2/3-21G level, and found that direct and indirect intermolecular hyperconjugations have no distinct difference, and intramolecular hyperconjugation and rehybridization are similar to those of the Cl^- and Br^- bifurcated H-bonds, the blue shifts of the I^- H-bonds can be explained by use of the same theory.

4 Conclusions

In this work we applied *ab initio* quantum chemistry methods to study the bifurcated H-bonds between the proton donors H_2CZ (Z=O, S, Se) and H_2CZ_2 (Z=F, Cl, Br) and the proton acceptor Cl^- and Br^-. The calculated results show that these bifurcated H-bonds are blue-shifted. In these systems, and the H-bonding angles are relatively small (104°~108°), and the H-bonding configuration is very bent. This bent configuration determines blue shift of the formed H-bond. We studied the topological properties of these systems using the theory of atoms in molecules, and found that they are similar with those of the linear H-bonds, so according to the definitions of H-bonds proposed by both Bader and Popelier, these intermolecular interactions are exactly H-bonding. The NBO analysis of these systems further explores the origins of blue-shifts of these bifurcated H-bonds. Summarily, we found that blue shifts of these bifurcated bent H-bonds are caused by three factors: (1) small direct intermolecular hyperconjugation but relatively larger indirect intermolecular hyperconjugation; (2) large decrease of intramolecular hyperconjugation; and (3) relatively large rehybridization. So the theory of inter- and intramolecular hyperconjugations and rehybridization can well interpret these blue-shifted H-bonds.

1 Scheiner S. Hydrogen Bonding. New York: Oxford University Press, 1997

2 Jeffrey G A. An Introduction to Hydrogen Bonding. New York: Oxford University Press, 1997

3 Desiraju G R, Steiner T. The Weak Hydrogen Bond. Oxford: Oxford University Press, 1999

4 Hobza P, Havlas Z. Blue-shifting hydrogen bonds. Chem Rev, 2000, 100(11): 4253－4264[DOI]

5 Alabugin IV, Manoharan M, Peabody S, Weinhold F. Electronic basis of improper hydrogen bonding: A subtle balance of hyperconjugation and rehybridization. J Am Chem Soc, 2003, 125(19): 5973－5987 [DOI]

6 Li A Y. Chemical origin of blue- and red-shifted hydrogen bonds: Intramolecular hyperconjugation and its coupling with intermolecular hyperconjugation. J Chem Phys, 2007, 126(15): 154102－154112 [DOI]

7 Rozas I, Alkorta I, Elguero J. Bifurcated hydrogen bonds: Three-centered interactions. J Phys Chem A, 1998, 102(48): 9925－9932 [DOI]

8 Li A Y. Theoretical investigation of hydrogen bonds between CO and HNF_2, H_2NF and HNO. J Phys Chem A, 2006, 110(37): 10805－10816[DOI]

9 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A, Vreven Jr T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C, and Pople J A. Gaussian 03. Pittsburgh PA: Gaussian, Inc., 2003

10 Boys S F, Bernardi F. The calculation of small molecular interactions by the differences of separate total energies: Some procedures with reduced errors. Mol Phys, 1970, 19(4): 553－566

11 Bader R F W. Atoms in Molecules: A Quantum Theory. Oxford: Claerndon Press, 1990

12 Biegler-König F. Calculation of atomic integration data. J Comp Chem, 2000, 21(12): 1040－1048

13 Biegler- König F. Software news and updates: AIM2000 —A program to analyze and visualize atoms in molecules. J Comp Chem, 2001, 22(5): 545－559

14 Biegler-König F. Software news and updates: Update of the AIM2000-Program for atoms in molecules. J Comp Chem, 2001, 23(15): 1489－1494[DOI]

15 Glendening E D, Badenhoop J K, Reed A E, Carpenter J E, Bohmann J A, Weinhold F. GenNBO5.0W, Theoretical Chemistry Institute, University of Wisconsin, Madison WI, 1996－2001

16 Tatamitani Y, Liu B, J. Shimada J, Ogata T, Ottavian P, Maris A, Caminati W, Alonso J L. Weak, improper, C—H⋯H—C hydrogen bonds in the dimethyl ether dimer. J Am Chem Soc, 2002, 124(11): 2739－2743[DOI]

17 Koch U, Popelier P L A. Characterization of C–H–O hydreogen bonds on the basis of the charge density. J Phys Chem, 1995, 99(24): 9747－9754