Interplay between H···O, H···X, X···O and X···X interactions in the complex pairing of formyl halides with hypohalous acids

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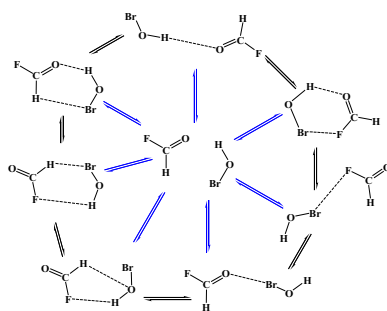
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HIGHLIGHTS

- Red and blue shift HB and XB interactions, formyl halides–hypohalous acids intermolecular complexes.

GRAPHICAL ABSTRACT

ABSTRACT

Ab initio study of the complexes formed by hypohalous acids (HOX, X = F, Cl, Br and I) with formyl halides (HCOY, Y = F, Cl, Br and I) has been carried out at the MP2/aug-cc-pVDZ computational level. These molecules can do a vast kind of H···O, H···X, X···O and X···Y interactions. The nature of the halogen atom in HOX is more important than HCOY in the X···Y interactions. Red shift of H–O bonds and blue shift of C–H bonds were observed frequently which are in line with the elongation (weakening) and contraction (strengthening) of related bonds, respectively. The interactions were analyzed with atoms in molecules (AIM) and natural bond orbital (NBO) theories. Results are showing good correlations between structural properties and AIM parameters.

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1. Introduction

Hypohalous acids (HOX, X = F, Cl, Br and I) are known to be strong oxidants, participating in oxidation, fluorination, epoxidation and hydroxylation processes [1]. Traces of chlorine and bromine containing molecules play important roles in many areas of atmospheric chemistry. The most notable one is the polar depletion of ozone concentration [2,3]. The reduction of ozone in the antarctic atmosphere during the austral spring is strongly related to the catalytic reactions involving chlorine substituted hydrocarbons. Among the halogens chlorine compounds are believed to be especially effective in promoting ozone loss in the lower stratosphere, and there is a great interest in species which can act as chlorine reservoirs. Formyl chloride (HCOCl) is an intermediate in the atmospheric degradation of several important chlorinated hydrocarbons, e.g., CH_3Cl, CH_2Cl_2, and C_2HCl_3 [2]. Formyl fluoride is proving to be a fruitful subject for studies of state-specific photo dissociation dynamic [4].

The investigations of non-covalent interactions, particularly hydrogen bond, are one of the most frequently studied aspects not only for their diverse molecular topologies, but also for their

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potential applications in varied fields such as chemistry, biology, physics, and so on. Many physicochemical properties of substances are determined by hydrogen bond interaction. Moreover, it can direct many chemical, physical, and biochemical processes. In recent years, a large number of experimental and theoretical studies on the structure, stability and thermodynamic properties have been performed on the hydrogen bond complexes [5].

A number of studies have been performed for the hydrogen-bonded clusters formed by the hypohalous acids with themselves [4] or with other molecules [6–8]. As known, the HOX (X = Y = F, Cl, Br, or I) are easily formed in the atmosphere [6] and the HCOY species are intermediated in the atmospheric degradation of some halogenated hydrocarbons [9,10]. Therefore, the title complexes in the present study are of great interest in the field of atmospheric chemistry relevant to the ecological aspects. To the best of our knowledge, neither theoretical nor experimental reports regarding the interaction between hypohalous acids and formyl halides are available in the literature. In the absence of the experimental information, a theoretical analysis of the existence of such complexes and their properties appears to be necessary to understand the interaction between them.

2. Computational methods

Calculations were performed using the Gaussian 03 system of codes [11]. The geometries of the isolated HOX and formyl halide molecules as well as HOX–formyl halide complexes were fully optimized at the MP2 level of theory [12] with the aug-cc-pVDZ basis set [13] for all atoms, except iodine, for which the DGDZVP [14,15] basis set was used. The contraction scheme of this basis set is (6s5p3d2f) for I atom. Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of the zero point energy (ZPE). The counterpoise procedure was used to correct the interaction energy for the basis set superposition error [16]. The AIM2000 package [17,18] and AIMAll [19] were used to obtain bond properties; and to plot molecular graphs. The natural bond orbital (NBO) method [20] has been used to analyze the interaction of occupied and empty orbitals with the NBO program supplied with Gaussian 03.

3. Results and discussion

The HOX molecules could have different types of hydrogen-bond and halogen-bond interactions with HCOY molecules. In summary, results of HOX–HCOY interactions has been denoted as XYm (m = 1–7), Fig. 1. In the XYm notation X is representing the HOX molecules (HOF, HOCl, HOBr, and HOI are defined as X = F, Cl, Br and I, respectively); Y illustrates the formyl halides (HCOF, HCOCl, HCOBr and HCOI are defined as Y = F, Cl, Br and I, respectively) and m was used to show the type of the complex. For example FF1 (X = F, Y = F, m = 1) is illustrating a type 1 complexation occurring between HOF and HCOF. Similarly, ClBr2 (X = Cl, Y = Br, m = 2) is used for a type 2 complex formation between HOCl with HCOBr.

Fig. 1 shows the possible ways which might be considered for the interaction of HCOY with HOX molecules. Results of the geometry optimizations on these proposed complexes have been restricted to the structures given in Tables 1–7, (S1–S5) and Figs. S1 and S2.

The proposed patterns which considered for HOX–HCOY interactions include hydrogen bonding (H···O, H···X, H···Y) and halogen bonding (X···Y, X···O), Fig. 1.

Results show the following order for stabilities of different types of complexes in the most cases: type (I) > type (IV) > type (VII) > type (II) > type (III) > type (V) > type (VI) (Tables 1–7).
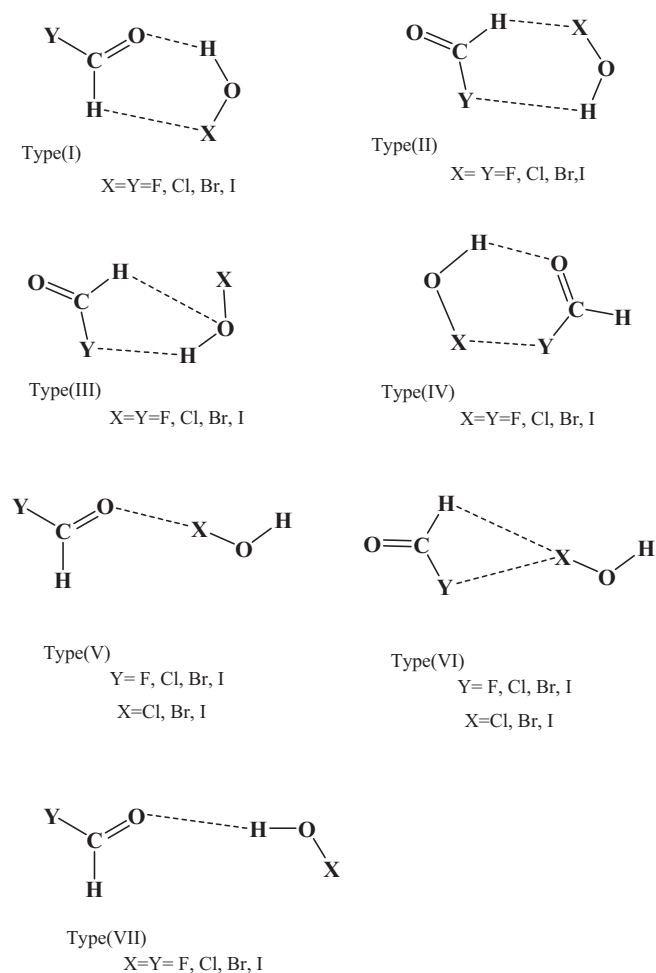

Fig. 1. Schematic representation of possible models for intermolecular interactions of HCOY with HOX molecules. Type (I) > type (IV) > type (VII) > type (II) > type (III) > type (V) > type (VI).

For example stabilities of HOF–HCOY and HOCl–HCOY complexes are in the order: FY1 > FY4 > FY7 > FY2 and ClY1 > ClY4 > ClY7 > ClY2 > ClY3 > ClY5 > ClY6 (for Y = F, Cl, Br).

The nature of the halogen atom in HCOY has a small effect on the stabilities of halogen-bond complexes whereas the nature of the halogen atom in HOX imposes a great impact on the stabilities of halogen-bond complexes. For instance in type (V), the stabilities of the XF5's are in the range of −2.40 to −4.60 kcal/mol, while those for ClY5's are close together (−2.40 to −3.00 kcal/mol), Table 5.

The electrostatic potential is an effective tool for analyzing and predicting of noncovalent interactions [6]. For electronic characteristics of the isolated monomers Fig. 2 shows two maxima in the molecular electrostatic potentials of HOCl, HOBr and HOI but one maximum in the molecular electrostatic potentials of HOF and HCOY (Y = F, Cl, Br and I). Also Fig. 3 displays the anisotropic charge distribution on the bromine atom for BrCl4, BrCl5 and BrCl6 complexes. This anisotropy could explain the electrophilic and nucleophilic character of halogen. For example, in the XY6 type halogen atom in HOX might simultaneously contribute in the HB (as Lewis base) and XB (as the Lewis acid) interactions.

Meanwhile in XY4 system although the molecular graphs show bond critical points (BCP) for X···Y, the dihalogen bond distance values are much longer than sum of the tabulated van der Waals radii for X and Y. Thus X···Y interaction between them does not found so dihalogen bond cannot be formed [21].

Table 1
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	FF1	ClF1	BrF1	IF1	FCl1	ClCl1	BrCl1	ICl1
BSSE	1.36	1.43	1.71	2.08	1.37	1.47	1.79	2.27
SE^{corr}	−4.97	−4.81	−4.86	−4.82	−4.92	−4.87	−5.00	−5.08
SE^{uncorr}	−6.48	−6.24	−6.24	−6.12	−6.35	−6.23	−6.31	−6.32
ΔE^{cp}	−3.61	−3.38	−3.15	−2.74	−3.55	−3.40	−3.21	−2.81
ν(C=O)	1801(279)	1801(281)	1801(275)	1800(267)	1732(355)	1732(370)	1732(368)	1731(361)
Δν(C=O)	−23	−24	−24	−25	−30	−30	−30	−31
Δr(C=O)	0.007	0.006	0.006	0.006	0.008	0.008	0.008	0.008
ν(H–C)	3203(4)	3197(4)	3195(5)	3193(5)	3146(1)	3140(2)	3138(2)	3135(2)
Δν(H–C)	26	20	18	16	26	21	19	16
Δr(H–C)	−0.002	−0.001	−0.001	−0.001	−0.002	−0.001	−0.001	−0.001
ν(Y–C)	1071(306)	1067(324)	1065(336)	1062(351)	777(258)	773(276)	771(287)	769(306)
Δν(Y–C)	49	45	43	40	40	40	37	34
Δr(Y–C)	−0.016	−0.015	−0.014	−0.014	−0.025	−0.023	−0.022	−0.022
ν(H–O)	3605(374)	3609(422)	3615(411)	3625(425)	3600(457)	3604(504)	3609(483)	3619(482)
Δν(H–O)	−142	−137	−129	−123	−147	−142	−134	−129
Δr(H–O)	0.008	0.007	0.007	0.006	0.008	0.007	0.007	0.007
ν(X–O)	943(2)	748(7)	654(24)	595(25)	943(2)	748(8)	654(12)	594(22)
Δν(X–O)	7	7	7	10	7	7	8	10
Δr(X–O)	0.003	−0.005	−0.007	−0.010	0.003	−0.004	−0.006	−0.010

	FBr1	ClBr1	BrBr1	IBr1	FI1	ClI1	BrI1	II1
BSSE	1.46	1.56	1.89	2.35	1.74	1.87	2.17	2.58
SE^{corr}	−4.85	−4.85	−5.01	−5.09	−5.03	−5.08	−5.23	−5.23
SE^{uncorr}	−6.23	−6.16	−6.26	−6.26	−6.37	−6.36	−6.45	−6.40
ΔE^{cp}	−3.39	−3.29	−3.12	−2.74	−3.29	−3.21	−3.06	−2.65
ν(C=O)	1726(421)	1726(442)	1726(443)	1725(437)	1712(522)	1712(554)	1712(557)	1710(552)
Δν(C=O)	−33	−33	−33	−34	−38	−38	−37	−39
Δr(C=O)	0.009	0.008	0.008	0.008	0.010	0.009	0.009	0.009
ν(H–C)	3129(1)	3123(1)	3121(1)	3118(1)	3105(1)	3099(1)	3096(1)	3091(1)
Δν(H–C)	26	20	18	15	27	20	17	13
Δr(H–C)	−0.002	−0.001	−0.001	−0.001	−0.002	−0.001	−0.001	−0.001
ν(Y–C)	683(215)	680(232)	679(240)	676(260)	604(191)	601(207)	600(217)	598(168)
Δν(Y–C)	33	30	29	26	31	28	27	25
Δr(Y–C)	−0.028	−0.026	−0.025	−0.024	−0.034	−0.032	−0.031	−0.030
ν(H–O)	3604(481)	3606(525)	3612(501)	3621(499)	3597(551)	3599(594)	3605(565)	3612(571)
Δν(H–O)	−143	−140	−131	−127	−150	−146	−138	−137
Δr(H–O)	0.007	0.007	0.007	0.006	0.008	0.007	0.007	0.007
ν(X–O)	943(2)	748(8)	654(14)	594(23)	943(2)	748(8)	654(12)	592(91)
Δν(X–O)	7	7	8	10	7	6	8	8
Δr(X–O)	0.003	−0.004	−0.006	−0.009	0.003	−0.004	−0.006	−0.009

[a] BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

Table 2
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	FF2	ClF2	BrF2	FCl2	FBr2	FI2
BSSE	1.09	1.20	1.52	1.54	2.02	2.64
SE^{corr}	−3.28	−3.10	−3.27	−3.62	−4.30	−4.87
SE^{uncorr}	−4.23	−4.02	−4.13	−4.58	−5.27	−5.82
ΔE^{cp}	−2.19	−1.90	−1.75	−2.08	−2.28	−2.23
ν(C=O)	1840(262)	1839(275)	1837(280)	1782(335)	1783(404)	1779(512)
Δν(C=O)	16	15	13	20	24	29
Δr(C=O)	−0.005	−0.005	−0.005	−0.005	−0.005	−0.006
ν(H–C)	3208(2)	3198(3)	3194(3)	3154(2)	3139(3)	3119(4)
Δν(H–C)	31	21	17	35	36	40
Δr(H–C)	−0.002	−0.001	−0.001	−0.002	−0.002	−0.002
ν(Y–C)	943(150)	946(271)	948(260)	693(217)	619(180)	552(157)
Δν(Y–C)	−79	−76	−74	−44	−31	−21
Δr(Y–C)	0.028	0.025	0.024	0.033	0.037	0.044
ν(H–O)	3692(198)	3694(236)	3694(234)	3661(148)	3636(183)	3585(273)
Δν(H–O)	−55	−52	−49	−86	−111	−162
Δr(H–O)	0.004	0.003	0.003	0.005	0.006	0.009
ν(X–O)	938(140)	746(7)	652(11)	936(3)	936(1)	934(1)
Δν(X–O)	2	5	6	0	0	−2
Δr(X–O)	0.002	−0.003	−0.005	0.003	0.003	0.004

[a] BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

Tables 1–7 and S3 present the H–O, O–X, H–C, C=O and C–Y stretching frequencies of HOX and HCOY free molecules as well as XY*m* complexes and also their shifts due to the intermolecular interactions. In the XY1 complexes the H–O and C=O bonds exhibit red shifts along with elongation. Red shifts of O–H bands are greater and their values are in agreement with stabilities of the

Table 3
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	ClF3	BrF3	IF3	ClCl3	BrCl3	ICl3	ClBr3
BSSE	1.31	1.62	2.03	1.67	2.00	2.57	2.18
SE^{corr}	−3.18	−3.44	−3.82	−4.03	−4.44	−4.98	−4.84
SE^{uncorr}	−4.17	−4.42	−4.74	−5.05	−5.44	−5.94	−5.88
ΔE^{cp}	−1.87	−1.82	−1.79	−2.36	−2.44	−2.41	−2.66
ν(C=O)	1834(250)	1832(251)	1830(264)	1781(325)	1780(324)	1779(331)	1784(392)
Δν(C=O)	10	8	6	19	18	17	25
Δr(C=O)	−0.004	−0.003	−0.003	−0.005	−0.005	−0.004	−0.005
ν(H–C)	3196(4)	3195(4)	3192(2)	3140(2)	3138(2)	3131(5)	3122(3)
Δν(H–C)	19	18	15	21	19	12	19
Δr(H–C)	−0.001	−0.001	−0.001	−0.001	−0.001	−0.000	−0.001
ν(Y–C)	959(236)	963(229)	965(227)	695(204)	695(199)	695(198)	620(169)
Δν(Y–C)	−63	−59	−57	−42	−42	−42	−30
Δr(Y–C)	0.021	0.020	0.020	0.032	0.032	0.033	0.038
ν(H–O)	3704(124)	3705(125)	3713(144)	3665(155)	3668(158)	3681(172)	3636(198)
Δν(H–O)	−42	−38	−35	−81	−75	−67	−110
Δr(H–O)	0.003	0.003	0.002	0.005	0.004	0.004	0.006
ν(X–O)	741(9)	647(14)	586(27)	740(9)	645(15)	585(27)	739(10)
Δν(X–O)	0	1	2	−1	−1	1	−2
Δr(X–O)	0.000	0.000	−0.001	0.001	0.001	0.000	0.001

	BrBr3	IBr3	FI3	ClI3	BrI3	II3
BSSE	2.51	3.07	2.63	2.96	3.28	3.59
SE^{corr}	−5.29	−5.83	−4.81	−5.62	−6.09	−6.47
SE^{uncorr}	−6.31	−6.82	−5.83	−6.71	−7.17	−7.49
ΔE^{cp}	−2.78	−2.76	−2.18	−2.66	−2.81	−2.88
ν(C=O)	1783(391)	1783(399)	1780(511)	1782(499)	1782(496)	1783(504)
Δν(C=O)	24	24	30	32	32	33
Δr(C=O)	−0.005	−0.005	−0.006	−0.007	−0.007	−0.007
ν(H–C)	3118(4)	3109(10)	3114(4)	3096(5)	3090(7)	3079(16)
Δν(H–C)	15	6	35	17	11	0
Δr(H–C)	−0.000	0.000	−0.002	−0.001	−0.000	0.001
ν(Y–C)	620(166)	620(165)	552(157)	553(149)	554(148)	555(150)
Δν(Y–C)	−30	−30	−21	-20	−19	−18
Δr(Y–C)	0.038	0.04	0.044	0.047	0.048	0.051
ν(H–O)	3640(200)	3654(217)	3588(257)	3579(315)	3583(319)	3603(338)
Δν(H–O)	−103	−94	−159	−167	−160	−145
Δr(H–O)	0.006	0.005	0.008	0.009	0.008	0.007
ν(X–O)	645(15)	585(28)	934(1)	739(10)	645(15)	585(27)
Δν(X–O)	−1	1	−2	−2	−1	1
Δr(X–O)	0.001	0.000	0.004	0.001	0.001	0.000

^a BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

Table 4
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	FF4	ClF4	BrF4	IF4	FCl4	ClCl4	BrCl4	ICl4
BSSE	1.15	1.18	1.35	1.63	1.30	1.36	1.53	1.88
SE^{corr}	−3.97	−4.02	−4.03	−4.10	−4.15	−4.36	−4.43	−4.55
SE^{uncorr}	−5.33	−5.35	−5.33	−5.36	−5.50	−5.70	−5.74	−5.82
ΔE^{cp}	−2.82	−2.84	−2.68	−2.47	−2.85	−3.00	−2.90	−2.67
ν(C=O)	1807(268)	1806(256)	1806(247)	1806(246)	1735(314)	1734(301)	1734(293)	1734(291)
$\Delta\nu$(C=O)	−17	−18	−18	−18	−27	−28	−28	−28
Δr(C=O)	0.006	0.006	0.006	0.005	0.008	0.008	0.008	0.008
ν(H–C)	3196(13)	3194(14)	3193(14)	3193(15)	3136(13)	3135(13)	3135(14)	3134(14)
$\Delta\nu$(H–C)	19	17	16	16	17	16	16	15
Δr(H–C)	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
ν(Y–C)	1069(248)	1065(239)	1063(235)	1061(231)	779(216)	776(208)	775(205)	773(202)
$\Delta\nu$(Y–C)	47	43	41	39	42	39	38	36
Δr(Y–C)	−0.020	−0.010	−0.010	−0.010	−0.030	−0.020	−0.020	−0.020
ν(H–O)	3643(364)	3636(418)	3637(410)	3646(455)	3628(367)	3620(416)	3622(411)	3631(447)
$\Delta\nu$(H–O)	−104	−110	−106	−102	−119	−126	−121	−117
Δr(H–O)	0.005	0.006	0.006	0.005	0.006	0.006	0.006	0.006
ν(X–O)	941(1)	747(9)	652(13)	593(25)	941(2)	747(10)	653(14)	593(25)
$\Delta\nu$(X–O)	5	6	6	9	5	6	7	9
Δr(X–O)	0.002	−0.004	−0.005	−0.008	0.002	−0.004	−0.005	−0.008

	FBr4	ClBr4	BrBr4	IBr4	FI4	ClI4	BrI4	II4
BSSE	1.48	1.57	1.76	2.08	1.67	1.80	1.97	2.13
SE^{corr}	−4.15	−4.45	−4.55	−4.66	−4.20	−4.55	−4.66	−4.65
SE^{uncorr}	−5.47	−5.75	−5.82	−5.89	−5.48	−5.82	−5.88	−5.83
ΔE^{cp}	−2.67	−2.88	−2.79	−2.58	−2.53	−2.75	−2.69	−2.52
ν(C=O)	1727(364)	1726(350)	1726(343)	1726(343)	1713(451)	1711(439)	1711(433)	1712(437)
$\Delta\nu$(C=O)	−32	−33	−33	−33	−37	−39	−39	−38
Δr(C=O)	0.009	0.009	0.008	0.008	0.009	0.009	0.009	0.009
ν(H–C)	3119(12)	3118(12)	3118(13)	3117(13)	3092(14)	3091(15)	3090(15)	3090(15)
$\Delta\nu$(H–C)	16	15	15	14	13	12	11	11
Δr(H–C)	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
ν(Y–C)	686(186)	684(180)	683(174)	682(172)	606(174)	606(168)	604(161)	603(152)
$\Delta\nu$(Y–C)	36	34	33	32	33	33	31	30
Δr(Y–C)	−0.030	−0.030	−0.030	−0.030	−0.040	−0.030	−0.030	−0.030
ν(H–O)	3628(348)	3620(394)	3622(391)	3632(429)	3625(348)	3614(401)	3616(400)	3626(449)
$\Delta\nu$(H–O)	−119	−126	−121	−116	−122	−132	−127	−122
Δr(H–O)	0.006	0.006	0.006	0.006	0.006	0.007	0.006	0.006
ν(X–O)	941(1)	747(8)	653(15)	593(25)	940(1)	747(9)	653(14)	592(31)
$\Delta\nu$(X–O)	5	6	7	9	4	6	7	8
Δr(X–O)	0.002	−0.003	−0.005	−0.008	0.002	−0.003	−0.005	−0.008

[a] BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

Table 5
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	ClF5	BrF5	IF5	ClCl5	BrCl5	ICl5
BSSE	0.90	1.50	2.30	1.00	1.70	2.60
SE^{corr}	−2.40	−3.70	−4.60	−2.70	−4.10	−5.10
SE^{uncorr}	−3.10	−4.40	−5.40	−3.30	−4.70	−5.80
ΔE^{cp}	−1.50	−2.20	−2.30	−1.70	−2.40	−2.50
ν(C=O)	1812(290)	1805(327)	1799(373)	1747(389)	1737(432)	1727(484)
Δν(C=O)	−12	−19	−25	−15	−25	−35
Δr(C=O)	0.002	0.004	0.006	0.003	0.006	0.008
ν(H–C)	3181(9)	3182(7)	3184(5)	3123(7)	3123(5)	3125(3)
Δν(H–C)	4	5	7	4	4	6
Δr(H–C)	0.000	0.000	0.000	−0.000	−0.000	−0.000
ν(Y–C)	1039(329)	1052(334)	1065(325)	753(241)	763(281)	776(290)
Δν(Y–C)	17	30	43	16	26	39
Δr(Y–C)	−0.006	−0.010	−0.014	−0.009	−0.016	−0.024
ν(H–O)	3745(80)	3746(90)	3755(108)	3745(86)	3746(97)	3755(115)
Δν(H–O)	−1	3	7	−1	3	7
Δr(H–O)	−0.000	0.000	−0.001	0.000	0.000	−0.001
ν(X–O)	730(24)	636(30)	576(51)	728(68)	634(43)	575(63)
Δν(X–O)	−11	−10	−8	−13	−12	−9
Δr(X–O)	0.005	0.005	0.005	0.005	0.006	0.006

	ClBr5	BrBr5	IBr5	ClI5	BrI5	II5
BSSE	1.00	1.70	2.60	1.20	1.90	2.60
SE^{corr}	−2.80	−4.10	−5.10	−3.00	−4.30	−5.20
SE^{uncorr}	−3.40	−4.70	−5.80	−3.50	−4.90	−5.80
ΔE^{cp}	−1.80	−2.40	−2.50	−1.80	−2.40	−2.60
ν(C=O)	1743(468)	1732(516)	1721(574)	1732(589)	1719(644)	1706(713)
Δν(C=O)	−16	−27	−38	−18	−31	−44
Δr(C=O)	0.004	0.006	0.009	0.004	0.007	0.01
ν(H–C)	3107(6)	3107(4)	3109(2)	3083(8)	3082(6)	3081(3)
Δν(H–C)	4	4	6	4	3	2
Δr(H–C)	−0.000	−0.000	−0.000	−0.001	−0.000	−0.000
ν(Y–C)	663(245)	673(214)	682(237)	586(212)	593(232)	602(173)
Δν(Y–C)	13	23	32	13	20	29
Δr(Y–C)	−0.010	−0.018	−0.028	−0.013	−0.023	−0.034
ν(H–O)	3744(89)	3745(101)	3754(119)	3744(93)	3745(106)	3754(125)
Δν(H–O)	−2	2	6	−2	2	6
Δr(H–O)	0.000	0.000	−0.001	0.000	0.000	−0.001
ν(X–O)	729(17)	634(63)	574(71)	728(24)	634(22)	573(112)
Δν(X–O)	−12	−12	−10	−13	−12	−11
Δr(X–O)	0.005	0.005	0.006	0.005	0.006	0.006

[a] BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

Table 6
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	ClF6	BrF6	IF6	ClCl6	BrCl6	ICl6
BSSE	0.70	1.34	1.82	0.96	1.70	2.36
SE^{corr}	−1.73	−2.49	−2.90	−2.44	−3.56	−4.17
SE^{uncorr}	−2.14	−2.93	−3.31	−2.95	−4.09	−4.69
ΔE^{cp}	−1.03	−1.15	−1.08	−1.48	−1.86	−1.81
ν(C=O)	1826(288)	1830(301)	1833(311)	1769(343)	1774(353)	1780(362)
Δν(C=O)	2	6	9	7	12	18
Δr(C=O)	−0.001	−0.002	−0.003	−0.002	−0.003	−0.005
ν(H–C)	3185(9)	3184(8)	3184(7)	3128(5)	3125(3)	3120(3)
Δν(H–C)	8	7	7	9	6	1
Δr(H–C)	−0.001	−0.000	−0.000	−0.000	−0.000	0.000
ν(Y–C)	997(266)	983(276)	970(284)	716(194)	710(211)	699(208)
Δν(Y–C)	−25	−39	−52	−21	−27	−38
Δr(Y–C)	0.008	0.013	0.017	0.013	0.020	0.027
ν(H–O)	3742(82)	3742(93)	3748(112)	3740(86)	3740(98)	3747(119)
Δν(H–O)	−4	−1	0	−6	−3	−1
Δr(H–O)	0.000	0.000	0.000	0.000	0.000	0.000
ν(X–O)	739(14)	645(18)	584(40)	734(41)	637(31)	577(49)
Δν(X–O)	−2	−1	0	−7	−9	−7
Δr(X–O)	0.001	0.000	0.000	0.003	0.003	0.003

	ClBr6	BrBr6	IBr6	ClI6	BrI6	II6
BSSE	1.32	2.14	2.80	1.59	2.49	2.72
SE^{corr}	−3.02	−4.39	−5.07	−3.37	−4.97	−5.13
SE^{uncorr}	−3.56	−4.93	−5.60	−3.93	−5.53	−5.69
ΔE^{cp}	−1.70	−2.25	−2.27	−1.78	−2.48	−2.41
ν(C=O)	1769(406)	1776(418)	1784(427)	1765(505)	1774(519)	1782(519)
Δν(C=O)	10	17	25	15	24	32
Δr(C=O)	−0.002	−0.004	−0.006	−0.003	−0.005	−0.007
ν(H–C)	3110(3)	3105(3)	3096(5)	3084(3)	3073(3)	3057(11)
Δν(H–C)	7	2	−7	5	−6	−22
Δr(H–C)	−0.000	0.000	0.001	0.000	0.001	0.002
ν(Y–C)	635(173)	624(106)	622(170)	564(149)	559(145)	554(121)
Δν(Y–C)	−15	−26	−28	−9	−14	−19
Δr(Y–C)	0.016	0.024	0.034	0.021	0.032	0.042
ν(H–O)	3740(88)	3740(100)	3747(122)	3738(91)	3738(105)	3745(127)
Δν(H–O)	−6	−3	−1	−8	−5	−3
Δr(H–O)	0.001	0.000	0.000	0.001	0.000	0.000
ν(X–O)	727(29)	636(108)	572(60)	715(43)	615(71)	569(98)
Δν(X–O)	−14	−10	−12	−26	−31	−15
Δr(X–O)	0.005	0.006	0.006	0.008	0.014	0.008

[a] BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

Table 7
The H-bond energies (SE^{uncorr}, SE^{corr}, BSSE and ΔE^{cp}) and some structural properties of HCOY···HOX complexes at MP2/aug-cc-pVDZ level.[a]

Complex	FF7	ClF7	BrF7	IF7	FCl7	ClCl7	BrCl7	ICl7
BSSE	1.11	1.09	1.19	1.75	1.32	1.32	1.45	1.99
SE^{corr}	−3.82	−3.83	−3.81	−3.94	−4.04	−4.12	−4.15	−4.34
SE^{uncorr}	−5.16	−5.10	−5.05	−5.28	−5.39	−5.40	−5.39	−5.68
ΔE^{cp}	−2.71	−2.74	−2.62	−2.19	−2.72	−2.80	−2.70	−2.35
ν(C=O)	1809(283)	1808(304)	1808(309)	1806(295)	1736(309)	1735(332)	1735(336)	1734(331)
Δν(C=O)	−15	−16	−16	−18	−26	−27	−27	−28
Δr(C=O)	0.005	0.005	0.005	0.005	0.007	0.007	0.007	0.008
ν(H–C)	3198(12)	3196(14)	3195(15)	3194(17)	3139(11)	3137(13)	3137(14)	3135(15)
Δν(H–C)	21	19	18	17	20	18	18	16
Δr(H–C)	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
ν(Y–C)	1059(246)	1059(240)	1058(235)	1060(223)	770(201)	771(197)	770(192)	772(189)
Δν(Y–C)	37	37	36	38	33	34	33	35
Δr(Y–C)	−0.01	−0.01	−0.01	−0.01	−0.02	−0.02	−0.02	−0.02
ν(H–O)	3657(385)	3644(526)	3643(549)	3649(608)	3642(350)	3625(543)	3624(578)	3630(631)
Δν(H–O)	−90	−102	−100	−99	−105	−121	−119	−118
Δr(H–O)	0.005	0.005	0.005	0.005	0.005	0.006	0.006	0.006
ν(X–O)	941(3)	747(9)	653(11)	596(25)	939(3)	745(6)	652(13)	595(23)
Δν(X–O)	5	6	7	12	3	4	6	11
Δr(X–O)	0.001	0.000	0.000	−0.010	0.002	0.000	0.000	−0.010

	FBr7	ClBr7	BrBr7	IBr7	FI7	ClI7	BrI7	II7
BSSE	1.52	1.52	1.65	2.21	1.80	1.81	1.95	2.38
SE^{corr}	−4.11	−4.22	−4.26	−4.46	−4.21	−4.34	−4.40	−4.54
SE^{uncorr}	−5.43	−5.45	−5.45	−5.75	−5.5	−5.56	−5.59	−5.79
ΔE^{cp}	−2.59	−2.70	−2.61	−2.25	−2.41	−2.53	−2.45	−2.16
ν(C=O)	1728(354)	1727(379)	1727(383)	1726(380)	1713(433)	1711(462)	1711(466)	1711(468)
Δν(C=O)	−31	−32	−32	−33	−37	−39	−39	−39
Δr(C=O)	0.008	0.008	0.008	0.008	0.009	0.009	0.009	0.009
ν(H–C)	3122(11)	3120(12)	3119(13)	3118(14)	3095(13)	3093(14)	3092(15)	3091(16)
Δν(H–C)	19	17	16	15	16	14	13	12
Δr(H–C)	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001	−0.001
ν(Y–C)	677(162)	678(156)	678(157)	679(153)	598(136)	598(130)	598(126)	600(132)
Δν(Y–C)	27	28	28	29	25	25	25	27
Δr(Y–C)	−0.020	−0.030	−0.030	−0.030	−0.030	−0.030	−0.030	−0.030
ν(H–O)	3641(315)	3624(520)	3623(559)	3629(617)	3631(312)	3612(536)	3611(581)	3618(645)
Δν(H–O)	−106	−122	−120	−119	−116	−134	−132	−130
Δr(H–O)	0.005	0.006	0.006	0.006	0.006	0.007	0.006	0.006
ν(X–O)	937(4)	744(9)	651(11)	594(22)	935(4)	743(8)	650(15)	591(18)
Δν(X–O)	1	3	5	10	−1	2	4	7
Δr(X–O)	0.002	0.000	0.000	−0.010	0.003	0.000	0.000	−0.010

[a] BSSE, SE^{corr}, SE^{uncorr} and, ΔE^{cp} in kcal mol^{-1}; ν in cm^{-1} and r in Å.

corresponding complexes. On the other hand, blue shifts and bond contractions were observed for C–H, C–Y and O–X bonds. For C–H and C–Y bonds these shifts are more considerable and in line with stabilities of the related complexes (Table1).

In the XY2 model (FF2, ClF2, BrF2, FCl2, FBr2 and FI2) ν$_{C=O}$ and ν$_{C–H}$ bands show blue shift while for ν$_{C–Y}$ and ν$_{H–O}$ red shift were observed. In the XF2 compounds the blue shifts of ν$_{C=O}$ and ν$_{C–H}$ and also red shifts of ν$_{C–Y}$ and ν$_{H–O}$ bands are in the same direction with stabilities of corresponding complexes. But for O–X bond of XF2 complexes small blue shifts were observed which increased from FF2 to ClF2 and BrF2. On the other hand, in the FY2 type complexes (Y = Cl, Br, I) the blue shifts of ν$_{C=O}$ and ν$_{C–H}$ bands and also red shift of ν$_{H–O}$ increased from Y = Cl to Br and I but in contrast red shift of ν$_{C–Y}$ decreased from Y = Cl to Br and I (Table 2).

In the XY3 complexes XF3, XCl3, XBr3 (X = Cl, Br, I) and XI3 (X = F, Cl, Br, I) were obtained. Blue shifting of C=O and C–H in contrast with red shift of C–Y and O–H bonds were observed. The magnitude of Δν are frequently in close dependence with binding energies of corresponding complexes (Table 3).

For the XY4 (X, Y = F, Cl, Br and I) complexes red shifts of ν$_{C=O}$ and ν$_{H–O}$ and blue shifts of ν$_{C–H}$, ν$_{C–Y}$ and ν$_{O–X}$ were observed (Table 4). These shifts mainly depend on the nature of Y functions and heavier Y atoms show smaller blue shifts for ν$_{C–H}$ and ν$_{C–Y}$. On the other hand, replacing of X for a certain Y leads to smaller ranges for Δν$_{C–Y}$. The ν$_{O–H}$ show −102 to −132 cm^{-1} red shifts in XY4 complexes which are greater than shift observed for the other

bands. Finally 4–9 cm^{-1} blue shifts were observed for O–X bond in the XY4 complexes.

In the XY5 complexes (X = Cl, Br, I and Y = F, Cl, Br, I) red shifts of ν$_{C=O}$ and ν$_{O–X}$ and blue shifts of ν$_{C–Y}$ and ν$_{C–H}$ were seen. In these complexes Δν$_{C=O}$ and Δν$_{C–Y}$ increased but Δν$_{O–X}$ decreased with increasing stabilities of corresponding complexes (Table 5). Results are indicating that X has a major importance on Δν$_{C=O}$ and Δν$_{C–Y}$, so that by replacing the X for a certain Y the Δν$_{C=O}$, Δν$_{C–Y}$, Δν$_{C–H}$ and Δν$_{O–H}$ increased but Δν$_{O–X}$ decreased with stabilities and heaviness of X atom in these complexes.

In XY6 complexes (X = Cl, Br, I and Y = F, Cl, Br, I) blue shifts of ν$_{C=O}$ and ν$_{C–H}$ (except of IBr6, BrI6, II6) and red shifts of ν$_{C–Y}$, ν$_{O–H}$ and ν$_{O–X}$ were seen, also they have greater Δν$_{C=O}$ and Δν$_{C–Y}$ for heavier X atoms (Table 6).

The XY7 complexes displayed red shifts of ν$_{C=O}$, ν$_{O–H}$ and blue shifts of ν$_{C–H}$, ν$_{C–Y}$ and ν$_{O–X}$ which these shifts have close dependence on Y. Blue shifts of ν$_{C–H}$ and ν$_{C–Y}$ decreased for heavier Y atoms. Effect of X is smaller than Y on Δν for XY7 systems. The ν$_{O–H}$ shows the greatest shifts among different bands in this model (Table 7).

4. AIM analyses

The atom in molecules (AIM) theory [17] is applied here to analyze the characteristics of the intermolecular bond critical points (BCP) in studied complexes. The parameters (ρ) the electronic
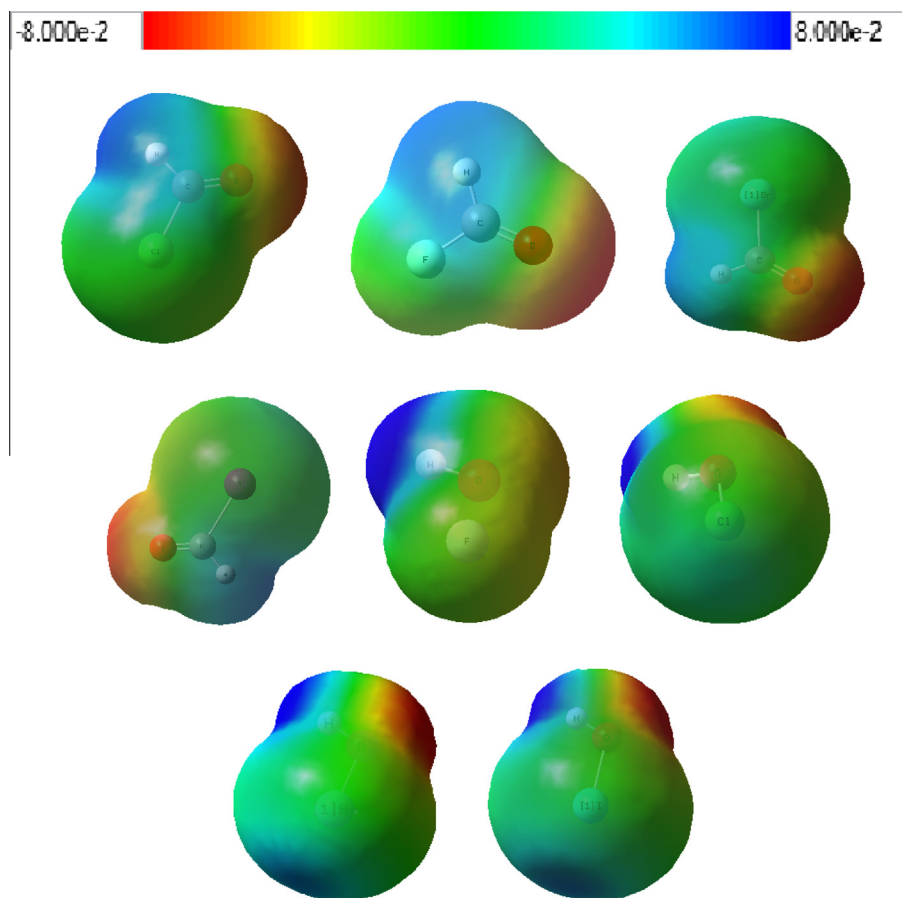
Fig. 2. Mp2/aug-cc-pVDZ. calculated 3D molecular electrostatic potential contour map of HCOY and HOX (X = Y = F, Cl, Br and I) The red color represents the minimal molecular electrostatic potential and the blue color denotes the maximal molecular electrostatic potential. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

density, ∇^2_{BCP} is Laplacian of electron density at BCP and H_{BCP} is the electron density at BCP and is the sum of the kinetic electron energy density (G_{BCP}) and the potential electron density (V_{BCP}), derived from the Bader theory also indicate the type of interaction. The negative value of the Laplacian of the electron density at BCP ($\nabla^2_{BCP} < 0$) designates the concentration of the electron charge in the region between the nuclei of the interacting atoms and is typical of covalent bonds-shared interactions. In the case of the ($\nabla^2_{BCP} > 0$), there is a depletion of the electron charge between atoms, indicating that there is an interaction of closed-shell systems like ions, van der Waals interactions, or H-bonds. Hence one can see that the Bader theory arbitrarily provides the characteristics of BCPs based on whether the interaction is covalent in nature. For a negative value of a Laplacian, there is no doubt about its covalence (from the AIM theory point of view). The interatomic and intermolecular interactions are also studied in terms of local electron energy density (H) and its components, the local kinetic electron energy density (G) and local potential electron energy density (V) at the BCPs. The relation between these energetic parameters is given in Eq. (1),

$$H = G + V \tag{1}$$

Further, from viral theorem that

$$\frac{1}{4}\nabla^2_{BCP} = 2G + V \tag{2}$$

Rozas et al. [22] suggested that both the Laplacian and the energy density should be used as criteria to characterize hydrogen bonding. They found that weak hydrogen-bonds show both, ∇^2_{BCP}

and $H > 0$; medium hydrogen-bonds show $\nabla^2_{BCP} > 0$ and $H < 0$, while strong ones show both ∇^2_{BCP} and $H < 0$. This classification seems to be suitable for halogen bonding too. For the complexes investigated here (Tables 8–11, all ∇^2_{BCP} at the H⋯O, X⋯Y, H⋯X, H⋯Y and X⋯O bond critical points are positive, and in most cases H at this BCP is positive. This means that these interactions belong to weak interactions. For H⋯I in FI2, FI3, ClI3, BrI3 and II3 complexes, H is negative, indicating medium interaction with a partially covalent nature.

The balance between the local kinetic electron energy density (G) and the local potential electron energy density (V) reveals the nature of the interaction. If the ratio $-G-V$ is greater than one, $\frac{-G}{V} > 1$, then the nature of the interaction is purely noncovalent. It can be seen for the most complexes the ratio of the kinetic electron energy density (G) and the potential electron energy density (V) are greater than one, $\frac{-G}{V} > 1$ which confirmed the existence of weak H-bond or X-bond interaction between the two systems and nature of the interaction is purely noncovalent. For H⋯I in FI2, FI3, ClI3, BrI3 and II3 complexes, $\frac{-G}{V} < 1$, indicating medium interactions with partially covalent in nature.

Topological parameters ρ and ∇^2_{BCP}, also describe the stability of complexes through the identification of charge density centers within the intermolecular bonds. Considering the results of the topological analysis presented in Tables 1–7 and S4 good agreement could be found between the values of the electronic density (ρ) and stabilization energy (SE) of HB complexes. Diagonalization of the Hessian of the electron density yields three eigenvalues ($\lambda 1$, $\lambda 2$ and $\lambda 3$). The ellipticity ($\varepsilon = (\lambda 1/\lambda 2) - 1$) measures the extent to
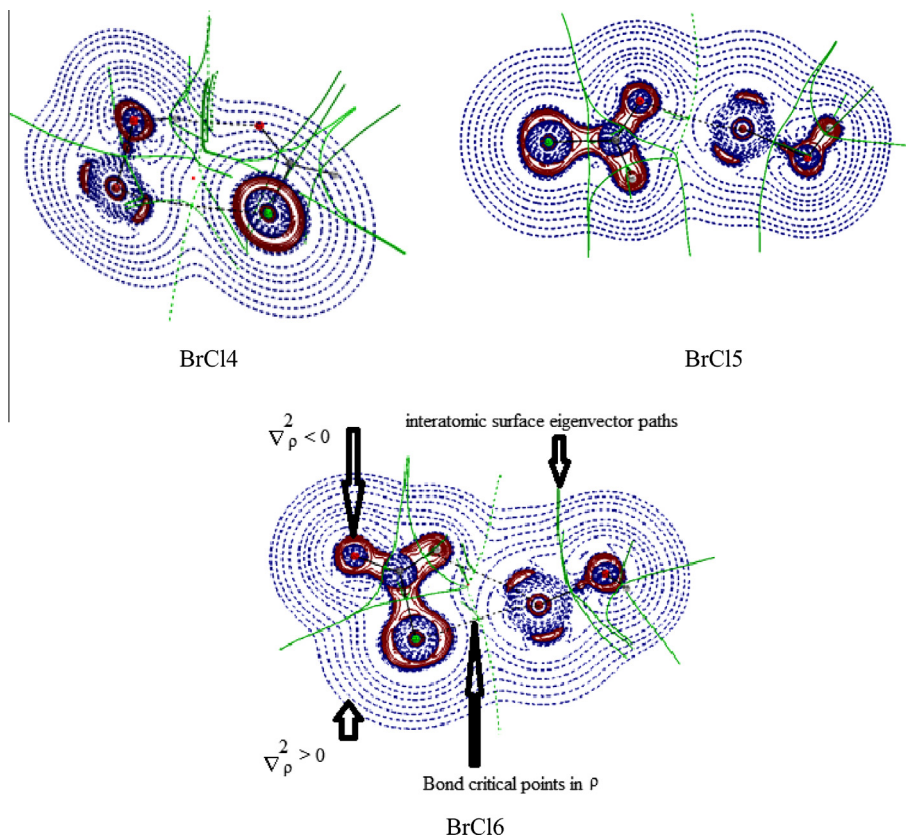
Fig. 3. Molecular graphs and contour maps of Laplacian of the electron density for BrCl4, BrCl5, BrCl6 complexes.

which charge is preferentially accumulated, thus it provides a measure for the stability of bond. Substantial bond ellipticity means that the bond can easily be ruptured [23]. The ellipticity of O3–I7, F3–Cl5, I6–I7, O3–H4, H5–Cl7, I6–F7 and H4–F6 bond critical points in II7, ClF4, II4, FI3, ClF6, IF4 and FI2 are (1.254, 0.928, 0.528, 0.475, 0.462, 0.391 and 0.390) very large, which supports those bonds are very weak, Tables 8–11 and S2 show the ellipticity at the intermolecular BCP. The interatomic distance for H···O and H···X interactions and the value of the Laplacian of electron density ∇^2_{BCP} at BCP show good relationship between the two parameters, Fig. S3.

Also, good linear relationship could be found between the electron density (ρ) at the BCP and the bond distance, d(O···X), in the XB complexes of HOCl, HOBr and HOI in the type (V), Fig. S4.

The electron density (ρ) at the BCP and the bond distance, d(H···X), in the HB complexes of HOF, HOCl, HOBr and HOI shows good linear relationship between two parameters, Fig. S5.

Also the electron density (ρ) at the BCP and the bond distance, d(H···O1) and d(H···O2), in the HB complexes of HOF, HOCl, HOBr and HOI shows good linear relationship between two parameters, Fig. 4.

5. Natural bond orbital analysis

Natural bond orbital (NBO) analysis [20] was performed on the minima found for the HCOY···HOX complexes, to elucidat charge-transfers (CT) in more detail. The results from this analysis at HF/aug-cc-pVDZ//MP2/aug-cc-pVDZ level of theory for the minima on the corresponding PESs are summarized in Tables 8–11. The NBO analysis stresses the role of intermolecular interaction in the complex, particularly charge transfer, the second-order

perturbation energy ($E^{(2)}$) can be taken as an index to judge the strength of intermolecular bonds. Tables 8–11 demonstrates the quantity of charge transferred from donor to the acceptor qCT and the second-order perturbation energy ($E^{(2)}$) due to the interaction of donor and acceptor orbital's. $E^{(2)}$ allow us to quantitatively evaluate the charge transfer involving the formation of the (HCOY···HOX) complexes. Furthermore, increase or decrease of the s-character in the O-atom hybrid orbital of the O–H bond well correlates with the strength of the interaction. For the stronger hydrogen bond the greater s-character is observed [24,25].

In the cyclic geometry of type (I) two charge transfers (CT) occurred, the first one is a lp(O_{HCOY}) → σ^*(O–H_{HOX}) CT that corresponds to HB interactions (Table 8). The $E^{(2)}$ values are dealing with greater dependency on this interaction to the nature of X atom. The Q_{CT} and $E^{(2)}$ of XY1 complexes (with same Y and different X atoms) are in line with their ΔE^{cp} but these correlations go to poorness for heavier X atoms. For this transition also good relationships were seen between $E^{(2)}$ and AIM parameters ρ and ∇^2.

The second CT in XY1 system is a weak lp(X_{HOX}) → σ^*(C–H_{HCOY}) transition that returns to the XB interaction (Table 8). The $E^{(2)}$ of these interactions decreases for heavier Y but increases for heavier X atoms. The relative magnitudes of $E^{(2)}$ for lp($O2_{HCOY}$) → σ^*(O–H_{HOX}) and lp(X_{HOX}) → σ^*(C–H_{HCOY}) charge transfers in XY1 complexes are dealing with greater contribution of the former one in the complex formation.

The $\Delta\nu_{H–O}$ is increased with increasing the $E^{(2)}$ of lp($O2_{HCOY}$) → σ^*(O–H_{HOX}) charge transfer and their relationship goes to poorness for heavier X atoms. Also $\Delta\nu_{C–H}$ is decreased with increasing the $E^{(2)}$ of lp(X_{HOX}) → σ^*(C–H_{HCOY}) transition.

The XY2 type complexes have both lp(Y) → σ^*(H–O) and lp(X) → σ^*(H–C) transitions. Natures of X and Y have different effect on these transitions so that $E^{(2)}$ of the first transition is

Table 8
Topological parameters and the NBO analysis of HCOY and HOX orbital's in [HCOY···HOX] complexes at MP2/aug-cc-pVDZ level of theory.[a]

Complex	FF1	ClF1	BrF1	IF1	FCl1	ClCl1	BrCl1	ICl1
qCT[b]	0.0117	0.0074	0.0048	0.0016	0.0125	0.008	0.0051	0.0009
$E^{(2)}$ LPO2 → σ*(O–H)	12.81	11.68	10.49	9.31	12.43	11.42	10.23	9.04
$E^{(2)}$ LPX → σ*(C–H)	0.79	1.15	1.46	1.63	0.67	1.03	1.35	1.97
$\nabla^2\rho$ BCP H–X	0.0342	0.0214	0.0203	0.0190	0.0342	0.0222	0.0213	0.0210
$\nabla^2\rho$ BCP O–H	0.1023	0.0993	0.0945	0.0906	0.1017	0.0990	0.0941	0.0899
G/V H–X	1.2584	1.2927	1.2592	1.2592	1.2490	1.2304	1.2639	1.1875
G/V O–H	1.1883	1.2072	1.2103	1.2149	1.2149	1.1841	1.2017	1.2064
H H–X	0.0015	0.0010	0.0009	0.0008	0.0013	0.0010	0.0008	0.0007
H O–H	0.0035	0.0036	0.0035	0.0034	0.0034	0.0036	0.0034	0.0033
ε H–X	0.161	0.054	0.008	0.031	0.115	0.012	0.024	0.058
ε O–H	0.059	0.034	0.027	0.023	0.06	0.034	0.027	0.022

	FBr1	ClBr1	BrBr1	IBr1	FI1	ClI1	BrI1	II1
qCT[b]	0.0124	0.0077	0.0048	0.0004	0.0132	0.0082	0.0052	0.0007
$E^{(2)}$ LPO2 → σ*(O–H)	11.99	11.02	9.87	8.73	12.18	11.24	10.10	9.08
$E^{(2)}$ LPX → σ*(C–H)	0.63	0.96	1.27	1.89	0.57	0.85	1.12	1.77
$\nabla^2\rho$ BCP H–X	0.0348	0.0229	0.0219	0.0215	0.0359	0.0241	0.0229	0.0223
$\nabla^2\rho$ BCP O–H	0.0999	0.0973	0.0924	0.0883	0.1013	0.0989	0.0940	0.0906
G/V H–X	1.2204	1.2559	1.2197	1.1742	1.1859	1.2311	1.1955	1.1405
G/V O–H	1.1836	1.2004	1.2027	1.2044	1.1811	1.1966	1.1994	1.2024
H H–X	0.0013	0.0010	0.0008	0.0007	0.0012	0.0010	0.0008	0.0006
H O–H	0.0034	0.0035	0.0033	0.0032	0.0034	0.0035	0.0034	0.0033
ε H–X	0.108	0.005	0.029	0.063	0.071	0.023	0.052	0.083
ε O–H	0.060	0.034	0.027	0.022	0.062	0.036	0.030	0.028

	FF2	ClF2	BrF2	FCl2	FBr2	FI2		
qCT[b]	0.0030	0.0013	0.0037	0.0046	0.0074	0.0166		
$E^{(2)}$ LPY → σ*(O–H)	6.66	5.81	5.06	6.57	8.22	11.04		
$E^{(2)}$ LPX → σ*(C–H)	2.03	2.28	2.88	2.61	2.63	1.91		
$\nabla^2\rho$ BCP H–Y	0.0781	0.0732	0.0684	0.0445	0.0400	0.0354		
$\nabla^2\rho$ BCP X–H	0.0356	0.0225	0.0212	0.0406	0.0420	0.0433		
G/V H–Y	1.1527	1.1675	1.1661	1.1242	1.0906	0.9963		
G/V X–H	1.1344	1.1959	1.1679	1.0952	1.0881	1.0966		
H H–Y	0.0023	0.0023	0.0021	0.0011	0.0008	−0.0000		
H X–H	0.0009	0.0008	0.0007	0.0008	0.0008	0.0009		
ε H–Y	0.080	0.051	0.044	0.064	0.063	0.058		
ε X–H	0.031	0.096	0.108	0.113	0.140	0.390		

[a] $E^{(2)}$ is in kcal mol^{-1} and qCT is in electron.
[b] qCT refers to the charge transferred between HCOY and HOX.

Table 9
Topological parameters and the NBO analysis of HCOY and HOX orbital's in [HCOY···HOX] complexes at MP2/aug-cc-pVDZ level of theory.[a]

Complex	ClF3	BrF3	IF3	ClCl3	BrCl3	ICl3	ClBr3
qCT[b]	0.0044	0.0055	0.0049	0.0006	0.0023	0.0032	0.0022
$E^{(2)}$ LPY → σ*(O–H)	2.28	1.75	1.47	4.97	4.11	3.10	6.89
$E^{(2)}$ LPO → σ*(C–H)	0.80	1.06	2.11	1.87	2.26	3.29	2.17
$\nabla^2\rho$ BCP O–H	0.0317	0.0338	0.0384	0.0382	0.0403	0.0454	0.0401
$\nabla^2\rho$ BCP Y–H	0.0560	0.0522	0.0490	0.0437	0.0423	0.0406	0.0410
G/V H–O	1.1688	1.1218	1.0578	1.0474	1.0301	1.0096	1.0318
G/V Y–H	1.0147	1.0182	1.0268	1.0956	1.0932	1.0928	1.0665
H H–O	0.0010	0.0008	0.0005	0.0004	0.0003	0.0001	0.0003
H Y–H	0.0002	0.0002	0.0003	0.0009	0.0008	0.0008	0.0006
ε H–O	0.053	0.019	0.028	0.014	0.011	0.009	0.012
ε Y–H	0.048	0.069	0.112	0.028	0.037	0.058	0.024

	BrBr3	IBr3	FI3	ClI3	BrI3	II3	
qCT[b]	0.0002	0.0011	0.0158	0.0118	0.0092	0.0058	
$E^{(2)}$ LPY → σ*(O–H)	6.00	4.67	10.88	10.63	9.50	7.31	
$E^{(2)}$ LPO → σ*(C–H)	2.63	3.82	1.52	2.43	2.93	4.26	
$\nabla^2\rho$ BCP O–H	0.0425	0.0485	0.0386	0.0428	0.0455	0.0519	
$\nabla^2\rho$ BCP Y–H	0.0402	0.0391	0.0354	0.0375	0.0372	0.0359	
G/V H–O	1.0179	1.0042	1.0976	1.0181	1.0077	1.0003	
G/V Y–H	1.0636	1.0617	0.9909	0.9773	0.9761	0.98	
H H–O	0.0002	0.0001	0.0008	0.0002	0.0001	0.0000	
H Y–H	0.0006	0.0005	−0.0001	−0.0002	−0.0002	−0.0002	
ε H–O	0.011	0.008	0.475	0.011	0.015	0.013	
ε Y–H	0.029	0.041	0.049	0.040	0.040	0.045	

[a] $E^{(2)}$ is in kcal mol^{-1} and qCT is in electron.
[b] qCT^a refers to the charge transferred between HCOY and HOX.

Table 10
Topological parameters and the NBO analysis of HCOY and HOX orbital's in [HCOY⋯HOX] complexes at MP2/aug-cc-pVDZ level of theory.[a]

Complex	FF4	ClF4	BrF4	IF4	FCl4	ClCl4	BrCl4	ICl4
qCT^b	0.0126	0.0108	0.0098	0.0096	0.0144	0.0130	0.0120	0.0118
$E^{(2)}$ LPO2 → σ*(O–H)	10.77	10.14	9.28	8.67	11.18	10.60	9.81	9.05
$\nabla^2\rho$ BCP H–O	0.0953	0.0933	0.0913	0.0887	0.0991	0.0975	0.0943	0.0928
$\nabla^2\rho$ BCP X–Y		0.0110		0.0099	0.0137	0.0105	0.0105	0.0098
G/V H–O	1.2428	1.2356	1.2419	1.2321	1.2349	1.2225	1.2184	1.2177
G/V X–Y		1.5289		1.6394	1.4143	1.2303	1.2124	1.2899
H H–O	0.0039	0.0037	0.0037	0.0035	0.0040	0.0038	0.0036	0.0035
H X–Y		0.0007		0.0007	0.0008	0.0004	0.0004	0.0005
ε H–O	0.042	0.025	0.026	0.016	0.039	0.018	0.011	0.005
ε X–Y		0.928		0.391	0.117	0.024	0.032	0.134
	FBr4	ClBr4	BrBr4	IBr4	FI4	ClI4	BrI4	II4
qCT^b	0.0143	0.0128	0.0119	0.0119	0.0148	0.0137	0.0128	0.0127
$E^{(2)}$ LPO2 → σ*(O–H)	10.92	10.36	9.59	8.88	10.91	10.64	9.89	9.17
$\nabla^2\rho$ BCP H–O	0.0983	0.0967	0.0936	0.0924	0.1005	0.1000	0.0971	0.0958
$\nabla^2\rho$ BCP X–Y	0.0140	0.0108	0.0107	0.0098	0.0136	0.0104	0.0099	0.0088
G/V H–O	1.2334	1.2199	1.2157	1.2147	1.2290	1.2168	1.2127	1.2137
G/V X–Y	1.3938	1.2223	1.2063	1.2865	1.4733	1.2969	1.2906	1.4252
H H–O	0.0039	0.0037	0.0035	0.0035	0.0039	0.0038	0.0036	0.0036
H X–Y	0.0008	0.0004	0.0004	0.0004	0.0008	0.0005	0.0005	0.0005
ε H–O	0.038	0.016	0.009	0.004	0.036	0.014	0.007	0.005
ε X–Y	0.135	0.041	0.036	0.211	0.090	0.056	0.062	0.528
	ClF5	BrF5	IF5	ClC5	BrCl5	ICl5		
qCT^b	0.0020	0.0073	0.0127	0.0026	0.0087	0.0144		
$E^{(2)}$ LPO2 → σ*(O–X)	2.49	5.13	8.21	2.67	5.54	8.95		
$\nabla^2\rho$ BCP O–X	0.0534	0.0608	0.0605	0.0560	0.0639	0.0638		
G/V O–X	1.1364	1.1120	1.0283	1.1322	1.1051	1.0173		
H O–X	0.0014	0.0014	0.0004	0.0015	0.0014	0.0003		
ε O–X	0.109	0.121	0.081	0.115	0.128	0.084		
	ClBr5	BrBr5	IBr5	ClI5	BrI5	II5		
qCT^b	0.0031	0.0088	0.0147	0.0034	0.0093	0.0156		
$E^{(2)}$ LPO2 → σ*(O–X)	2.60	5.46	8.92	2.68	5.66	9.21		
$\nabla^2\rho$ BCP O–X	0.0558	0.0637	0.0638	0.0572	0.0651	0.0649		
G/V O–X	1.1323	1.1053	1.0167	1.1291	1.1008	1.0130		
H O–X	0.0015	0.0014	0.0003	0.0015	0.0014	0.0002		
ε O–X	0.117	0.131	0.082	0.120	0.134	0.091		

[a] $E^{(2)}$ is in kcal mol^{-1} and qCT is in electron.
[b] qCT refers to the charge transferred between HCOY and HOX.

decreased for heavier X but for second one it is increased for heavier X (Table 8). In contrast $E^{(2)}$ of the lp(Y) → σ*(H–O) is increased for heavier Y but $E^{(2)}$ of lp(X) → σ*(H–C) is decreased for heavier Y atoms. Data are dealing with a relatively linear correlation between $E^{(2)}$ and ρ for lp(Y) → σ*(H–O) transition (Table 8).

In XY3 systems the lp(Y) → σ*(H–O) and lp(O$_{HOX}$) → σ*(H–C) transitions were observed. The variations of binding energies of two transitions are in opposite directions. For a certain Y the first CT tends to be weaker for heavier X while in the second CT an opposite order was seen. On the other hand, in the complexes with the same X and various Y, increasing of binding energies for greater Y was observed. Also comparison of NBO data with that of AIM shows that variation of their parameters are in contrast with each other which means that increasing of $E^{(2)}$ is along with decreasing of ρ and ∇^2 (Table 9).

For XY4 system, the NBO including lp(O$_{HCOY}$) → σ*(H–O) transitions with the same Y, the $E^{(2)}$ is effectively decreased for the heavier X but with same X the $E^{(2)}$ is not changed for different Y considerably. Also, high agreement between NBO ($E^{(2)}$) and AIM parameters (ρ and ∇^2) could be observed from the related results (Table 10).

The XY5 model (X = Cl, Br, I and Y = F, Cl, Br, I) has a lp(O$_{HCOY}$) → σ*(O–X) transition which its $E^{(2)}$ is increased for the heavier X, while replacing of Y has no sizable changes on $E^{(2)}$ (Table 10). On the other hand, good agreement could be found

between $E^{(2)}$ and ρ and ∇^2 parameters specially for $E^{(2)}$ versus ρ which has a linear relationship. This orbital interaction can be used to explain the elongation and red shift of X–O bonds [26].

In XY6 the lp(Y) → σ*(X–O) and lp(X) → σ*(H–C) transitions were occurred in which the former one could be known as dominant interaction, thus responsibility of X is greater than Y in complex formation. In this type good relationship was found between the second order energy, $E^{(2)}$, of lpY(HCOY) → σ*(O–X) and the frequencies shift of ($\Delta v/cm^{-1}$) of C=O, C–Y, O–X bonds and also ρ parameter.

The XY7 complexes are products of lp(O$_{HCOY}$) → σ*(O–H$_{HOX}$) transitions and $E^{(2)}$ of these transitions are in the same order for different X and Y. This seems reasonable since electron donation property of lp(O$_{HCOY}$) as well as electron acceptor ability of σ*(O–H$_{HOX}$) is less affected by Y and X which are away from them.

6. Conclusions

The HOX and HCOY (X, Y = F, C1, Br, I) molecules have expand of selections (including H⋯O, X⋯Y, H⋯X, H⋯Y and X⋯O interactions) for complexation which their stabilities depends on nature of X and Y. The association of H–O in hydrogen bonding is often along with bond lengthening and red shift, while blue shifts along with bond contractions were frequently observed for C–H bonds. The AIM results are dealing with noncovalent intermolecular

Table 11
Topological parameters and the NBO analysis of HCOY and HOX orbital's in [HCOY···HOX] complexes at MP2/aug-cc-pVDZ level of theory. [a]

Complex	ClF6	BrF6	IF6	ClCl6	BrCl6	ICl6
qCT[b]	0.0035	0.0015	0.0004	0.0000	0.0069	0.0096
$E^{(2)}$ LPY → σ*(O–X)	0.90	2.04	2.65	2.47	5.31	8.03
$E^{(2)}$ LPX → σ*(C–H)	1.01	1.02	1.14	1.78	1.96	2.73
$\nabla^2 \rho$ BCP H–X	0.0216			0.0262	0.0255	0.0257
$\nabla^2 \rho$ BCP Y–X	0.0419	0.0495	0.0452	0.0375	0.0445	0.0413
G/V H–X	1.3538			1.2258	1.2054	1.1396
G/V Y–X	1.1940	1.1558	1.1124	1.2557	1.2338	1.1322
H H–X	0.0011			0.0010	0.0009	0.0007
H Y–X	0.0015	0.0015	0.0010	0.0016	0.0018	0.0011
ε H–X	0.462			0.182	0.334	0.211
ε Y–X	0.122	0.141	0.105	0.151	0.161	0.126

	ClBr6	BrBr6	IBr6	CII6	BrI6	II6
qCT[b]	0.0030	0.0137	0.0174	0.0090	0.0314	0.0235
$E^{(2)}$ LPY → σ*(O–X)	3.41	7.29	10.90	4.69	11.20	12.30
$E^{(2)}$ LPX → σ*(C–H)	1.99	2.24	3.40	2.31	2.60	4.69
$\nabla^2 \rho$ BCP H–X	0.0279	0.0273	0.0278	0.0314	0.0306	0.0308
$\nabla^2 \rho$ BCP Y–X	0.0377	0.0442	0.0400	0.0357	0.0426	0.0328
G/V H–X	1.2062	1.1809	1.0971	1.1763	1.1482	1.0385
G/V Y–X	1.2324	1.1999	1.0897	1.1633	1.0940	1.0510
H H–X	0.0010	0.0009	0.0006	0.0010	0.0009	0.0003
H Y-X	0.0015	0.0016	0.0008	0.0011	0.0008	0.0004
ε H–X	0.150	0.249	0.123	0.067	0.139	0.004
ε Y–X	0.139	0.144	0.117	0.085	0.082	0.079

	FF7	ClF7	BrF7	IF7	FCl7	ClCl7	BrCl7	ICl7
qCT[b]	0.0125	0.0123	0.0118	0.0123	0.0151	0.0153	0.0151	0.015
$E^{(2)}$ LPO2 → σ*(O–H)	10.20	10.20	9.58	9.19	10.30	10.70	10.20	9.64
$E^{(2)}$ LPY → σ*(O–X)					0.10	0.07	0.09	0.29
$\nabla^2 \rho$ BCP O–H	0.0916	0.0933	0.0915	0.0920	0.0931	0.0972	0.0959	0.0964
G/V O–H	1.2615	1.2503	1.2462	1.2193	1.2324	1.2245	1.2208	1.2031
H O–H	0.0039	0.0039	0.0038	0.0035	0.0037	0.0038	0.0037	0.0035
ε O–H	0.049	0.038	0.034	0.039	0.064	0.053	0.050	0.048

	FBr7	ClBr7	BrBr7	IBr7	FI7	CII7	BrI7	II7
qCT[b]	0.0153	0.0155	0.0154	0.0155	0.0168	0.0172	0.0172	0.0173
$E^{(2)}$ LPO2 → σ*(O–H)	9.90	10.40	9.97	9.51	10.30	11.00	10.60	9.99
$E^{(2)}$ LPY → σ*(O–X)	0.23	0.15	0.17	0.43	0.37	0.23	0.28	0.57
$\nabla^2 \rho$ BCP O–H	0.0915	0.0962	0.0950	0.0963	0.0953	0.1009	0.1002	0.1011
G/V O–H	1.2269	1.2212	1.2177	1.2007	1.2257	1.2173	1.2136	1.1991
H O–H	0.0036	0.0037	0.0036	0.0034	0.0037	0.0038	0.0037	0.0036
ε O–H	0.064	0.053	0.050	0.047	0.065	0.054	0.050	0.048

[a] $E^{(2)}$ is in kcal mol^{-1} and qCT is in electron.
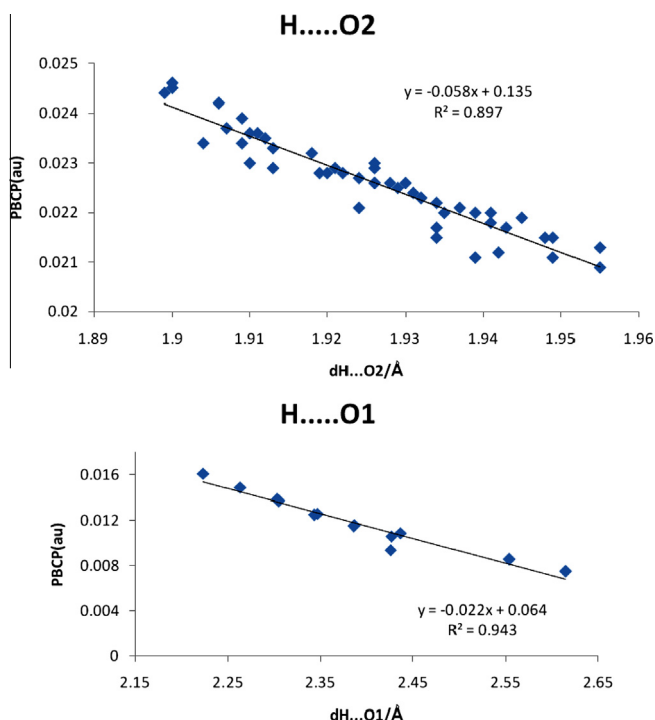[b] qCT refers to the charge transferred between HCOY and HOX.

Fig. 4. Relationship between the interatomic distance (Å) and the value of the electronic density (ρ) at BCP (a.u.) for H$\cdots$O interactions.

interactions in the most cases. The electrostatic interactions of halogen σ-hole and the electronegative halogen bond donors are responsible for the high degree of directionality exhibited by halogen bonds. Halogen atoms of HOCl, HOBr and HOI could participate in the hydrogen and halogen bond simultaneously which might arise from the presence of two maxima in the molecular electrostatic potentials of these molecules.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.07.047.

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