CODEN IEJMAT *Internet Electronic Journal of Molecular Design* **2006**, *5*, 331–344 ISSN 1538–6414
BioChem Press http://www.biochempress.com

Inter*net* **Electronic** Journal of
Molecular Design

June 2006, Volume 5, Number 6, Pages 331–344

Editor: Ovidiu Ivanciuc

Special issue dedicated to Professor Lemont B. Kier on the occasion of the 75th birthday

Resonance Energy and Intramolecular Hydrogen Bond Strength in 2–Halo–Phenols and 2,4–Dihalo–Malonaldehyde. A Theoretical Study

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Received: February 27, 2006; Revised: April 26, 2006; Accepted: May 7, 2006; Published: June 30, 2006

Citation of the article:

G. Buemi, Resonance Energy and Intramolecular Hydrogen Bond Strength in 2–Halo–Phenols and 2,4–Dihalo–Malonaldehyde. A Theoretical Study, *Internet Electron. J. Mol. Des.* **2006**, *5*, 331–344, http://www.biochempress.com.

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Resonance Energy and Intramolecular Hydrogen Bond Strength in 2–Halo–Phenols and 2,4–Dihalo–Malonaldehyde. A Theoretical Study [#]

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Internet Electron. J. Mol. Des. **2006**, *5* (6), 331–344

Abstract

Motivation. Aim of the paper is to examine the ring opening, ring closure and π–delocalization energy terms of the title compounds in order to account for the different trend of the hydrogen bridge strength with the halogen atom electronegativity on changing the basis set adopted for its evaluation. Such terms were obtained through partition of the hydrogen bond energy according to an extension of the approach suggested by Grabowski.

Method. Geometries and energies were calculated by the *ab initio* method using several basis sets of different extension and the G03W computation package.

Results. Analysis of the obtained results evidences that the ring opening energy terms predicted by the simplest basis sets show opposite trend with respect to those predicted by the more extended bases. The ring closure energies correlate very well with the hydrogen bond strength. It seems that the less extended bases overestimate the energy of the strained chelate ring. Excellent agreement is found between the experimental stretching mode frequencies of the OH group and the theoretical ones calculated at B3LYP/6–311++G(d,p) level. The HOMO surfaces of the chelate and open conformations are also presented.

Conclusions. E_{HB} correlates with the OH frequency shifts better than with the electronegativity of the halogens series and agree with the experimental estimates deduced from the temperature dependence of the infrared OH stretching band intensities better than with those estimated from the far IR OH rotational frequencies.

Keywords. 2–Halophenols; dihalomalonaldehyde; hydrogen bond; π–delocalization energy; OH anharmonic frequency.

Abbreviations and notations

ARB, Actual Rotation Barrier	E_{HB}, Hydrogen Bond Energy
RB, Rotation Barrier	DFT, Density Functional Theory
HOMO, Highest Occupied Molecular Orbital	NHOMO, Next to HOMO

1 INTRODUCTION

The phenolic derivatives (flavones and flavonoids, phenolic acids and so on) are a class of compounds having antioxidant properties being able to curtail radical species and to suppress oxidative damages. For such reason they are involved in many biological reactions, are essential for

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[#] Dedicated to Professor Lemont B. Kier on the occasion of the 75th birthday.

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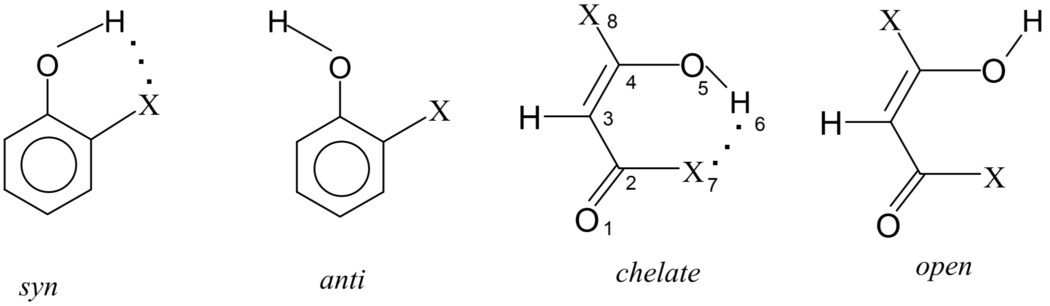
sustaining life and for foodstuffs conservation. Phenols and chlorinated phenols are widespread pollutants of waste and natural waters, and 2–bromosubstituted as well as 2–chlorosubstituted phenols are reported as precursors of dibenzodioxins. Mono–halophenols are very interesting for their chemical physical properties, mainly bound to inter and intramolecular interactions. In particular, the *syn* conformation is the most stable structure of *ortho*–halophenols (Figure 1) because it is stabilized by a weak intramolecular hydrogen bond involving the halogen atom. The strengths of these bridges (E_{HB}) were deduced from the OH rotational frequencies obtained from far IR rotational spectra [1] and from the temperature dependence of the infrared OH stretching band intensities [2,3]. Even if these latter estimates differ by about a factor of 2 with respect to those coming from the rotational constants, both of them indicate that the hydrogen bond energies are rather small, very close to each other and decrease on decreasing the electronegativity power of the halogen atom.

The OH stretching mode frequencies, measured in gas phase [3] and in dilute CCl_4 solution [4], decrease progressively on going from 2–F– to 2–Cl–, 2–Br– and 2–I–phenol, in agreement also with coherent anti–Stokes Raman Spectroscopy measurements [5], whereas the $\Delta\nu$ with respect to the corresponding frequency of the *anti* conformations increase on passing from 2–F– to 2–I–Phenol. On this ground, according to the Badger–Bauer rule [6], but in contrast with the above cited experimental findings, also E_{HB} should increase in the same direction. To account for these anomalous trends, many theoretical papers have been published in the last years.

Ab initio calculations carried out at various levels of sophistication, with and without correlation energy inclusion [7–10 and therein], gave contrasting results. In particular, the decrease of E_{HB} on decreasing the electronegativity power of the halogen atom is predicted only by the 3–21G, CEP–121G and LAN2DZ basis sets, whilst more extended bases, as the 6–31G, 6–31G** and 6–311++G(d,p), predicted E_{HB} increasing in the order $F \leq Cl < Br$, independently of the correlation energy inclusion. Also at higher level of calculations (cc–pVDZ, cc–pVTZ, aug–cc–pVDZ, aug–cc–pVTZ, cc–pVQZ, G2MP2, CBS–QB3) no satisfactory correlation between E_{HB} and electronegativity was evidenced, but the resulting E_{HB} values for various haloderivatives become nearly equal to each other (*e.g.*, at MP2/cc–pVDZ level 12.04 and 12.18 kJ/mol was found for 2–Cl–Phenol and 2–Br–Phenol, respectively, whereas G2MP2 approach predict 12.47 and 12.60 kJ/mol, respectively [7]) so suggesting that, very likely, the halogen electronegativity is not the only and main factor governing the interactions inside this type of chelate rings. On the other hand, it has been also pointed out that electronegativity, OH stretching mode frequency shift and hydrogen bond strength may not be correlated [5,11].

Results paralleling the above ones were obtained also for the $O–H\cdots X$ bonds of some theoretically possible conformations of 2,4–dihalo–malonaldehyde shown in Figure 1, for which, however, experimental findings cannot be available. Such conformations were previously taken into account [7,8] and are here revisited because they show the same anomalies observed in ortho–halophenols, notwithstanding their E_{HB} is substantially higher than in halo–phenols owing that a six–membered chelate ring is involved.



X = F, Cl, Br, I

Figure 1. Molecules and conformations taken into account in the present study.

The situation of ortho–halophenols has been interpreted in terms of the Electron Localization Function (ELF) in the excellent paper of Silvi *et al.* [12]. Remembering, with Larry Burggraf, that “the numbers are meaningless, but the trends are important”, it is interesting to understand why contrasting trends are theoretically predicted on increasing the basis set extension. In other words, it may exist somewhat a property that is strongly depending on the adopted basis set: this could be the resonance energy, which in the title compounds is expected to be very limited. For this aim, the approach recently suggested by Grabowski [13,14], which allows to partition E_{HB} in two energetic contributions (π–delocalization energy and ring closure energy), is here adopted, although it is to be remembered that the H–bond strength is the results of a balance of several energetic contributions strictly interconnected and therefore their partition is hard and approximate.

2 CALCULATIONS

Among the numerous basis sets tested in [7], the HF/3–21G, HF/3–21G*, HF/cc–pVQZ, MP2/LANL2DZ, MP2/6–311++G(d,p), B3LYP/6–31G** and B3LYP/6–311++G(d,p) results are here analyzed. Among them, only the 3–21G, 3–21G* and LANL2DZ bases allows to handle the iodine atom, too. All calculations were performed by means of the G03W computation package [15–18], running on a Pentium IV personal computer under XP operating system. No correction for the zero point vibration energy is here made since some conformations utilized for estimating the π–delocalization terms are saddle points and consequently a normal mode having negative frequency is present in the IR results. The IR spectra were calculated following the anharmonic model included in the same G03W program, which is able to give very good results [19–23] without scale factor corrections. Great caution must be exercised when the anharmonic model is used for IR frequencies calculations and the use of the "tight" or, better, "very tight" options are always and highly advisable. They do not improve significantly neither the calculated molecular geometry nor the total energy or harmonic frequencies, but certainly can help to avoid anomalous anharmonic values. Notwithstanding this, the Author was obliged to do numerous attempts, with noticeable time consuming, for obtaining correct anharmonic results for 2–Cl–phenol and 2–Br–phenol when B3LYP/6–311++G(d,p) calculations were carried out. In addition, the HOMO surfaces of each chelate and open conformation were built up by means of the GaussView 3.07 program.

3 METHOD

The strength of an intramolecular hydrogen bond (E_{HB}) is generally assumed to be the stability difference between the open and chelate conformations. According to Grabowski [13,14], the changing of the open conformation into the chelate one can be partitioned in two stages. The first stage is the 180° rotation of the OH group around the C–O single bond, the second is the consequent modification of the geometry and π–electron delocalization of the system. E_{HB} is therefore the sum of two terms: the former is the $|\Delta E|$ between the energy of the open conformation (E_O) and the energy of the chelate one having the same geometry (E'), i.e. it is the energy gained on passing from the open to the chelate form without geometry changes ("ring closure energy").

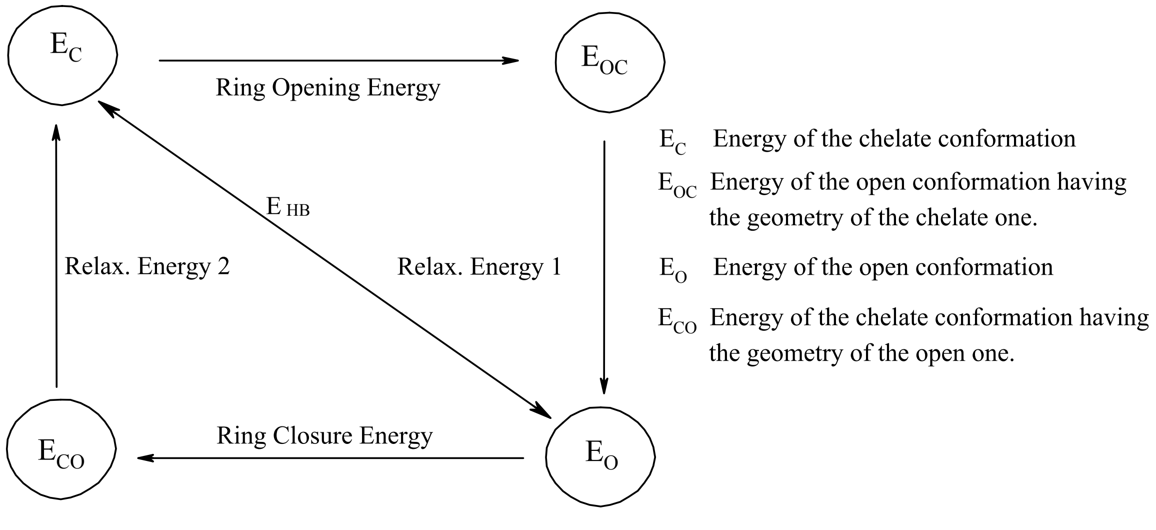


Figure 2. Scheme defining the various term of E_{HB} partitioning.

The second term is the $|\Delta E|$ between E' and the energy of the chelate conformation after full optimization (E_C), i.e. it is the energy gained by the system as consequence of the readjustment of its geometry and electronic structure. It was seen that such gain is mainly due to the "π–delocalization". Following the same procedure, one can define a "ring opening energy" (E''), as difference between the energy of the open conformation preserving the geometry of the chelate form (E_{OC}) and the energy of this latter one (E_C). Similarly, the energy difference between the non–optimized (E_{OC}) and optimized open conformations (E_O) is the "π–delocalization" energy of the open form. Also in this case the algebraic sum of the ring opening ($E_{OC}-E_C$) and the related π–delocalization energy is the hydrogen bond energy, E_{HB}. The entire cycle is schematized in Figure 2. Obviously, owing to the above definitions, the sum of the side–wall energies must vanish.

4 RESULTS AND DISCUSSION

The experimentally detected hydrogen bond strengths and the OH stretching mode frequencies of 2–halophenols available in the literature are shown in Table 1, together with the unscaled harmonic and anharmonic frequencies, calculated both at B3LYP/6–31G** and B3LYP/6–311++G(d,p) levels.

The predicted anharmonic frequencies are in very good agreement with the experimental findings, and an average of about 200 cm^{-1} red shifted with respect to those obtained according to the harmonic model. Good results were also obtained when the 6–31G** basis and B3LYP functional were used, whereas completely disappointing are those (here unreported) predicted by the simple HF/3–21G and B3LYP/3–21G basis sets. As it can be easily seen from Table 1, the Δν with respect to the value of the parent phenol, as well as the Δν between the *syn* and *anti* conformations, increases on decreasing the electronegativity of the halogen, just as experimentally observed. According to the qualitative correlation between Δν and hydrogen bond strength, this latter should therefore increase as electronegativity decreases, in opposition to the experimental findings reported in [1,3].

Table 1. Experimental and calculated OH frequencies (cm^{-1}, harmonic values reported in parentheses) and literature hydrogen bond energies (kJ/mol) of ortho–halophenols

	ν_{OH} (rot) Gas [a]	ν_{OH}(vib.) Gas [b]	ν_{OH}(vib.) Gas [c]	E_{HB} [a]	E_{HB} [b]	OH stretching mode frequencies B3LYP	
						6–31G**	6–311++G(d,p)
Phenol	310 [d]	3653	3657 [e]	–	–	3626 (3822)	3636 (3836)
2–F–Ph *syn*	379 (19.75)	3635	3636	6.82	–	3608 (3793)	3630 (3808)
anti	342	–	3656			3631 (3827)	3645 (3838)
2–Cl–Ph *syn*	407 (22.84)	3583	3584	6.82	14.27	3553 (3762)	3565 (3767)
anti	373	3645	3655	–	–	3651 (3824)	3637 (3836)
2–Br–Ph *syn*	404 (22.59)	3562	3554	6.40	13.10	3512 (3725)	3541 (3740)
anti	372	3646	3656	–	–	3630 (3823)	3645 (3834)
2–I–Ph *syn*	386 (20.79)	3538		5.52	11.51	–	–
anti	357	3647	–	–	–	–	–

[a] Ref. [1] (from far infrared spectra). The OH rotation barriers are reported in parentheses.
[b] Ref. [3] Values deduced from the temperature dependence of the infrared OH stretching band intensities.
[c] Ref. [5]. [d] Ref. [24]. [e] Ref. [25]. For a detailed *ab initio* study see Ref. [26].

The energy contributions to E_{HB}, obtained according to the Grabowski partition scheme at different levels of calculation, are collected in Tables 2 and 3. Analysis of data in Table 2 points out that, according to HF/3–21G and MP2/LANL2DZ predictions, the ring opening energy ($E_{OC}-E_C$) decreases on decreasing the electronegativity of the halogen atom involved in the hydrogen bridge whereas the ring closure energy ($E_{CO}-E_O$) increases in the same direction, reaching positive values for the Iodine–derivatives.

Table 2. Hydrogen bond energy partition terms (values in kJ/mol)

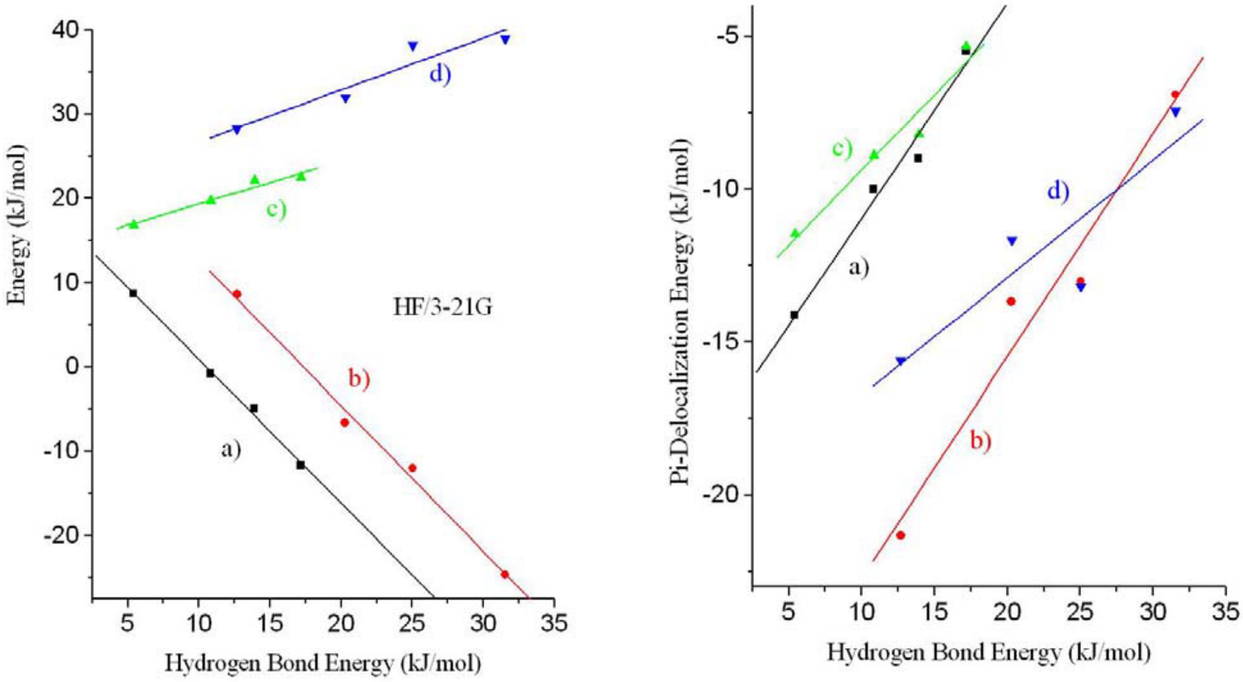
Compound	Ring Opening Energy ($E_{OC}-E_C$)	π–delocalization Energy [a] (E_O-E_{OC})	Ring Closure Energy ($E_{CO}-E_O$)	π–delocalisation Energy [b] (E_C-E_{CO})	E_{HB} [c]
			HF/3–21G		
2–F–Phenol	22.50	−5.32	−11.71	− 5.47	17.18
2–Cl–Phenol	22.10	−8.20	− 4.90	− 9.00	13.90
2–Br–Phenol	19.71	−8.90	− 0.81	−10.00	10.82
2–I–Phenol	16.86	−11.46	+ 8.71	−14.11	5.40
Malonaldehyde	79.93	−13.52	−53.34	−13.07	66.40
2,4–F–MDA	38.99	− 7.44	−24.65	− 6.90	31.55
2,4–Cl–MDA	38.21	−13.18	−12.02	−13.01	25.03
2,4–Br–MDA	31.95	−11.66	− 6.62	−13.67	20.29
2,4–I–MDA	28.28	−15.60	+ 8.64	−21.32	12.68
			HF/3–21G*		
2–F–Phenol	22.50	− 5.32	−11.71	− 5.47	17.03
2–Cl–Phenol	20.39	− 8.31	− 2.97	− 9.11	12.08
2–Br–Phenol	22.23	− 7.67	− 6.02	− 8.54	14.56
2–I–Phenol	17.99	−10.76	+ 5.78	−13.01	7.23
Malonaldehyde	79.93	−13.52	−53.34	−13.07	66.40
2,4–F–MDA	38.99	− 7.44	−24.65	− 6.90	31.55
2,4–Cl–MDA	27.53	−10.71	− 4.38	−12.44	16.82
2,4–Br–MDA	31.34	− 9.18	−11.50	−10.66	22.16
2,4–I–MDA	26.79	−12.96	+ 3.64	−17.47	13.83
			MP2/LANL2DZ		
2–F–Phenol	23.28	− 6.27	−10.78	− 6.23	17.01
2–Cl–Phenol	21.48	− 8.06	− 4.98	− 8.44	13.42
2–Br–Phenol	20.26	− 8.86	− 1.88	− 9.52	11.40
2–I–Phenol	18.37	− 9.92	+ 2.83	−11.27	8.44
Malonaldehyde	64.19	−11.39	−41.40	−11.39	52.80
2,4–F–MDA	40.55	−12.02	−18.57	− 9.95	28.52
2,4–Cl–MDA	38.38	−14.29	−11.29	−12.80	24.09
2,4–Br–MDA	34.93	−13.50	− 8.64	−12.79	21.43
2,4–I–MDA	32.72	−13.86	− 4.50	−14.36	18.86

[a] For the open conformation. [b] For the chelate conformation. [c] Without ZPVE correction.

This means that the opening of the chelate ring becomes progressively easier (owing to the hydrogen bond strength weakening) and the ring closure more difficult (perhaps for steric effect) on decreasing eletronegativity and on increasing the dimension of the halogen atom. On the same time, the obtained trends suggest the presence of increasing repulsive terms and/or strain in the chelate ring up to overcome the energy gain due to the π–delocalization (which, in turn, becomes progressively more negative on passing from fluorine to iodine). To be noted that the π–delocalization energy of the chelate ring is practically equal to that of the open conformation, (E_O–E_{OC}), except for the Br– and I–derivatives. Analogous considerations may be made for hydrogen bridges of the halogenated conformers of malonaldehyde, except at MP2/LANL2DZ level, where the π–delocalization terms of Br and I are closer to each other than those of F and Cl.

Figure 3–a shows that, at HF/3–21G level, the ring closure as well as the ring opening energies correlate very well with the hydrogen bond strengths of 2–halophenols, slightly less well in the case of MDA–derivatives (there is not a perfect proportionality). The strict interdependence between the π–delocalization energy concerning the chelate conformation and E_{HB} is clearly evident looking at Figure 3–b. The π–delocalization energies as regards the open forms show a still worse correlation, as, on the other hand was predictable since in these cases the hydrogen bond is lacking.

The 3–21G* basis differs from the 3–21G one for inclusion of polarization functions on Cl, Br and I. Its results modify the trends discussed above for Cl and Br. In particular, the ring closure energy of 2–Cl–phenol becomes about 2 kJ/mol less negative with respect to that of the 3–21G basis, whilst in 2–Br–phenol the ring closure energy becomes about 5 kJ/mol more negative and the π–delocalization contribution about 1.5 kJ/mol less negative than predicted in absence of polarization functions, with the conclusion that for Bromine a hydrogen bridge stronger than that involving Chlorine is predicted. The trend does not change in the MDA analogues.



(*a*) (*b*)

Figure 3. (*a*) Correlation between ring closure (black line = halophenols, red line = MDA derivatives) and ring opening (green line = halophenols, blue line = MDA derivatives) energies and the hydrogen bond strength. (*b*) Correlation between the π–delocalization (black line = halophenols, red line = MDA derivatives, chelate form) and the hydrogen bond strength. The green line (halophenols) and blue line (MDA derivatives) show the analogous correlation for the open form.

Inspection of the results obtained by the more extended basis sets (Table 3) points out that, differently from the previous cases, the ring opening energy increases on decreasing the electronegativity of the halogen atom, whereas the delocalization energy decreases as in the previous cases.

Table 3. Hydrogen bond energy partition terms (values in kJ/mol)

Compound	Ring opening Energy (E_{OC}–E_C)	π–delocalisation Energy [a] (E_O–E_{OC})	Rig closure Energy (E_{CO}–E_O)	π–delocalisation Energy (E_C–E_{CO}) [b]	$\lvert E_{HB}\rvert$ [c]
HF/cc–pVQZ					
2–F–Phenol	14.74	−4.00	−6.78	−3.95	10.74
2–Cl–Phenol	17.17	−4.86	−7.29	−5.01	12.30
2–Br–Phenol	19.32	−7.85	−5.51	−5.96	11.47
Malonaldehyde	53.51	−8.54	−36.94	−8.03	44.97
2,4–F–MDA	21.84	−4.81	−12.30	−4.73	17.03
2,4–Cl–MDA	21.38	−6.10	−9.10	−6.18	15.27
2,4–Br–MDA	23.25	−7.72	−7.62	−7.92	15.54
MP2/6–311++G(d,p)					
2–F–Phenol	15.93	−4.68	−6.60	−4.65	11.24
2–Cl–Phenol	16.50	−5.55	−5.21	−5.74	10.95
2–Br–Phenol	17.78	−6.02	−5.33	−6.42	11.75
Malonaldehyde	64.84	−14.03	−39.34	−11.47	50.81
2,4–F–MDA	30.91	−7.61	−16.51	−6.79	23.30
2,4–Cl–MDA	31.56	−9.88	−12.59	−9.08	21.68
2,4–Br–MDA	35.08	−10.17	−15.74	−9.17	24.91
B3LYP/6–31G**					
2–F–Phenol	17.08	−3.98	−9.05	−4.05	13.10
2–Cl–Phenol	18.14	−5.14	−7.55	−5.45	13.00
2–Br–Phenol	21.93	−5.36	−10.79	−5.77	16.56
Malonaldehyde	82.70	−19.86	−47.52	−15.32	62.84
2,4–F–MDA	35.74	−8.23	−20.58	−6.96	27.51
2,4–Cl–MDA	38.65	−10.92	−18.84	−8.84	27.72
2,4–Br–MDA	45.15	−11.53	−24.08	−9.54	33.62
B3LYP/6–311++G(d,p)					
2–F–Phenol	16.35	−4.14	−8.06	−4.16	12.22
2–Cl–Phenol	17.77	−4.86	−7.90	−5.01	12.91
2–Br–Phenol	18.47	−5.07	−8.04	−5.36	13.40
Malonaldehyde	70.85	−16.72	−40.23	−13.90	54.13
2,4–F–MDA	32.88	−8.40	−17.33	−7.15	24.48
2,4–Cl–MDA	36.97	−10.94	−16.95	−9.08	26.04
2,4–Br–MDA	38.50	−10.81	−19.12	−9.57	28.69

[a] For the open conformation. [b] For the chelate conformation. [c] Without ZPVE correction.

The trend of the ring closure energy does not show linear correlation with electronegativity. The main difference between the previously considered less extended bases and the most extended ones is therefore in the evaluation of the ring opening energy terms, whose effects, in turn, are reflected in the π–delocalization energy and E_{HB} values. These effects can be accounted for assuming different approximation in the strain and/or repulsions terms inside the chelate ring, which appear to be overestimated by the less extended bases. A further support to this interpretation is the analysis of the O···X distances in the chelate and open conformations, respectively.

Data reported in Table 4 show that in the halophenols (and some MDA derivatives) open conformations, $r_{O\ldots X}$ is shorter than in the chelate ones, whilst opposite trend should be obtained if one remembers that the hydrogen bridge tends to push the two heteroatoms closer to each other. On the whole, the $r_{O\ldots X}$ shortening predicted by the largest bases is lower than found at HF/3–21G and MP2/LANL2DZ level and for 2–halophenols it is larger than found in the halogenated derivatives of malonaldehyde, where (less strained) hexatomic rings are formed.

Table 4. O···O distances (Å) in the chelate and open conformations at various calculation levels [a]

	$r_{O\ldots X}$		$\Delta r_{O\ldots X}$	$r_{O\ldots X}$		$\Delta r_{O\ldots X}$
	Chelate	Open		Chelate	Open	
	HF/cc–pVQZ			HF/3–21G		
2–F–Phenol	2.7043	2.6500	–0.0543	2.7086	2.6667	–0.0419
2–Cl–Phenol	2.9955	2.9171	–0.0784	3.0509	2.9287	–0.1222
2–Br–Phenol	3.1160	3.0244	–0.0916	3.1526	3.0136	–0.1390
2–I–Phenol	–	–	–	3.3450	3.1614	–0.1836
2,4–F–MDA	2.6619	2.6748	+0.0129	2.5362	2.6162	+0.0800
2,4–Cl–MDA	3.0170	2.9764	–0.0406	2.9920	2.9286	–0.0634
2,4–Br–MDA	3.1420	3.0864	–0.0556	3.1456	3.0332	–0.1124
2,4–I–MDA	–	–	–	3.3870	3.1862	–0.2008
Malonaldehyde	2.6834	2.8879	+0.2045	2.6053	2.8335	+0.2282
	MP2/6–311++G(d,p)			HF/3–21G*		
2–F–Phenol	2.7368	2.6757	–0.0611	2.7086	2.6667	–0.0419
2–Cl–Phenol	3.0019	2.9099	–0.0920	3.0263	2.9001	–0.1262
2–Br–Phenol	3.1153	3.0170	–0.0983	3.1130	2.9934	–0.1196
2–I–Phenol	–	–	–	3.3191	3.1442	–0.1749
2,4–F–MDA	2.6260	2.6742	+0.0482	2.5362	2.6162	+0.0800
2,4–Cl–MDA	2.9267	2.9343	+0.0076	3.0219	2.9112	–0.1107
2,4–Br–MDA	3.0496	3.0359	–0.0137	3.0903	2.9905	–0.0998
2,4–I–MDA	–	–	–	3.3260	3.1580	–0.1680
Malonaldehyde	2.5846	2.8560	+0.2714			
	B3LYP/6–31G**			MP2/LAN2DZ		
2–F–Phenol	2.7107	2.6718	–0.0389	2.8290	2.7613	–0.0677
2–Cl–Phenol	3.0161	2.9330	–0.0831	3.1354	3.0132	–0.1222
2–Br–Phenol	3.1093	3.0299	–0.0794	3.2570	3.1134	–0.1436
2–I–Phenol	–	–	–	3.4050	3.2295	–0.1755
2,4–F–MDA	2.5904	2.6611	+0.0707	2.6247	2.7595	+0.1348
2,4–Cl–MDA	2.9447	2.9589	+0.0142	3.0320	3.0157	–0.0163
2,4–Br–MDA	3.0158	3.0473	+0.0315	3.1696	3.1202	–0.0494
2,4–I–MDA	–	–	–	3.3419	3.2342	–0.1077
Malonaldehyde	2.5533	2.8651	+0.3118	2.7172	2.9674	+0.2502
	B3LYP/6–311++G(d,p)			Van der Waals radii [b]		
2–F–Phenol	2.7320	2.6820	–0.0500	H	1.20 Å	
2–Cl–Phenol	3.0115	2.9326	–0.0789	O	1.52 Å	
2–Br–Phenol	3.1203	3.0385	–0.0818	F	1.47 Å	
2,4–F–MDA	2.6165	2.6965	+0.0800	Cl	1.75 Å	
2,4–Cl–MDA	2.9343	2.9627	+0.0284	Br	1.85 Å	
2,4–Br–MDA	3.0525	3.0674	+0.0149	I	1.98 Å	
Malonaldehyde	2.5879	2.9004	+0.3125			

[a] The MP2/6–311++G(d,p) and B3LYP/6–311++G(d,p) results give the best agreement with the available experimental O···F distance of ortho–fluoro–phenol reported in Ref. [33]. [b] Ref. [27].

Since this fact should affect also the π–delocalization energy, it is interesting to examine the π–delocalization energies of MDA and those of the other compounds, relatively to their chelate conformations. The O–H···O strength in the unsubstituted MDA is roughly twice that predicted for the strongest O–H···Halogen bridge (*i.e.*, the O–H···F one), whatever is the basis set adopted for calculations. It is therefore expected that also its π–delocalization energy should be higher than that of the corresponding haloderivatives in general, and of 2–halophenol in particular, since in this latter case one has a pentatomic chelate ring. Consequently, it appears to be strange that the π–delocalization energy predicted by the less extended basis sets for 2,4–Cl–MDA and 2,4–Br–MDA is higher than that of the parent compound. This does not occur with the most extended bases, although at HF/cc–pVQZ level the difference between MDA and 2,4–Br–MDA is less than 1 kJ/mol. In conclusion, it seems that the E_{HB} dependence from the electronegativity is a questionable argument, whilst, according to the Badger–Bauer rule, a good correlation with the experimental and calculated Δν's of the OH stretching mode frequencies is observed.

Finally, it is interesting to point out that (analogously to the ring opening and ring closure energy terms) the OH rotation barrier (RB) includes the hydrogen bond energy and its value can be considered as sum of the actual OH rotation barrier (ARB) plus the energy required for the hydrogen bond breaking (E_{HB}), so that it can be written [27] as

$$RB = ARB + E_{HB}$$

This formula allows to calculate E_{HB} from the rotation barrier and it has been successfully used in many cases [28–32 and references therein], including the molecules discussed here [8].

5 HOMO ORBITAL SHAPES

The progressive increase of the atomic dimension on going from fluorine to iodine implies an increase in the principal quantum number (*i.e.*, an increase in the space filled by the charge distribution) of the atomic orbitals contributing to the molecular orbitals of the title compounds, so it could be interesting to examine the shape of highest occupied MO and its evolution in the haloderivatives series. The surfaces of the 2–X–phenols and 2,4–X–malonaldehyde HOMOs, derived from B3LYP/6–311++G(d,p) calculations and obtained by means of the GaussView 3.07 program, are shown in Figures 4 and 5, respectively.

The HOMOs of 2–halo–phenols, having π nature, show similar contours and evidence the different dimensions of the halogen atoms. For the 2,4–dihalo–malonaldehyde conformations the HOMO surface contours are similar for all compounds except for the bromine–derivatives.

In this molecule, the HOMO of the chelate conformation evidences a strong interaction with the hydroxyl hydrogen whereas that of the open form has a quite different shape because it is a σ–

orbital with a strong n–component of the bromine and oxygen atoms (Br_7 and O_5). What occurred is an interchange between HOMO and NHOMO on passing from the chelate to the open conformation. Such interchange does not occur when the results of the simple HF/3–21G basis are analyzed.

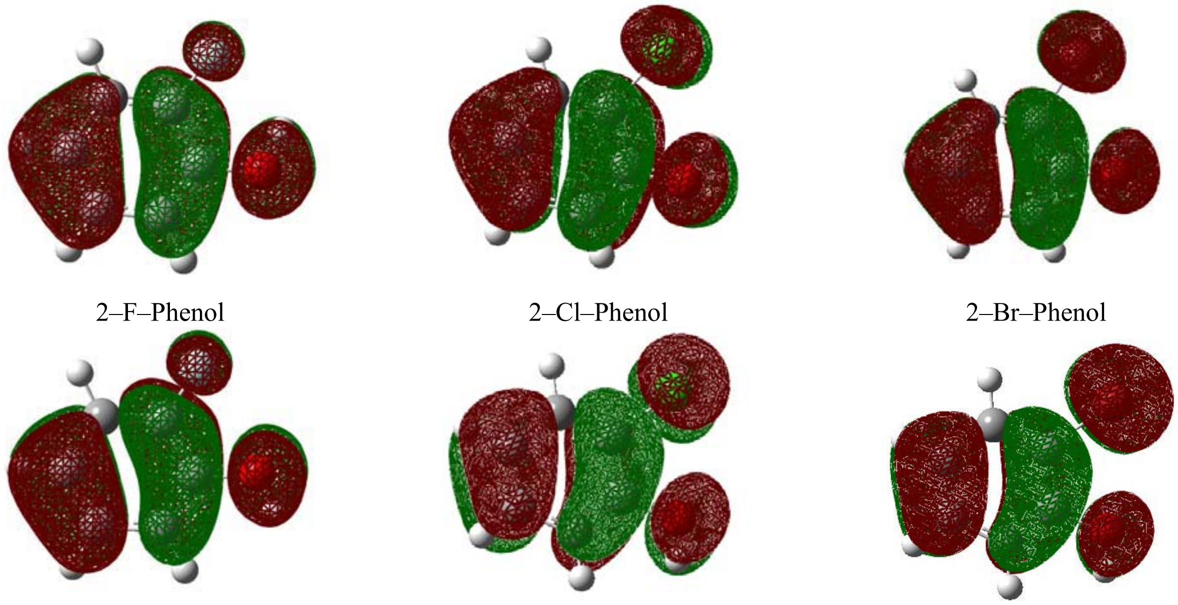

2–F–Phenol 2–Cl–Phenol 2–Br–Phenol

Figure 4. HOMO surfaces of 2–halo–phenols. Top: chelate conformations; bottom: open conformations.

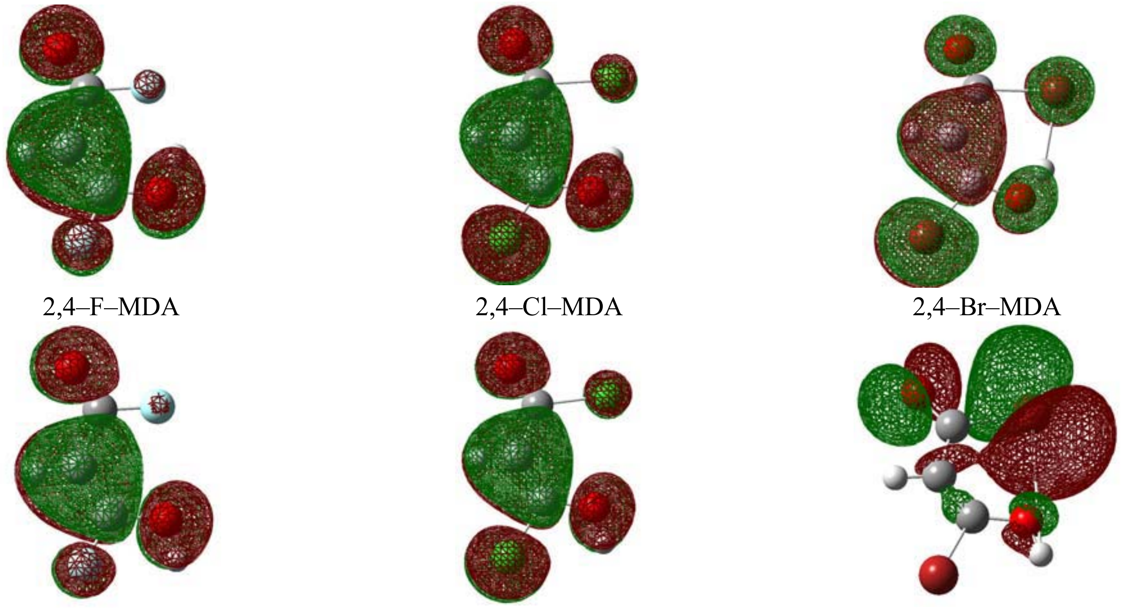

2,4–F–MDA 2,4–Cl–MDA 2,4–Br–MDA

Figure 5. HOMO surfaces of 2,4–dihalo–malonaldehydes. Top: chelate conformations; bottom: open conformations.

The HOMO surfaces of 2–Br– and 2–I–phenol as well as those of 2,4–Br– and 2,4–I–MDA, coming from the simple HF/3–21G* basis set are shown in Figure 6. For 2–halophenols no substantial difference appears with respect to the shape of the B3LYP/6–311++G(d,p) orbitals. On the contrary, in the chelate and open conformations of 2,4–Br–MDA no contribution of the Br_9 atomic orbital is evidenced. Similarly, in the HOMO of the chelate form of 2,4–I–MDA there is a scarce contribution of the atomic orbitals of the bridged atoms whereas the HOMO of the open form has *n*–nature and it is quite entirely localized on I_9 atom. The situation is analogous to that found in 2,4–Br–MDA at B3LYP/6–311++G(d,p) level. On the whole, these surface contours can partially justify the E_{HB} trend predicted by the 3–21G basis set.

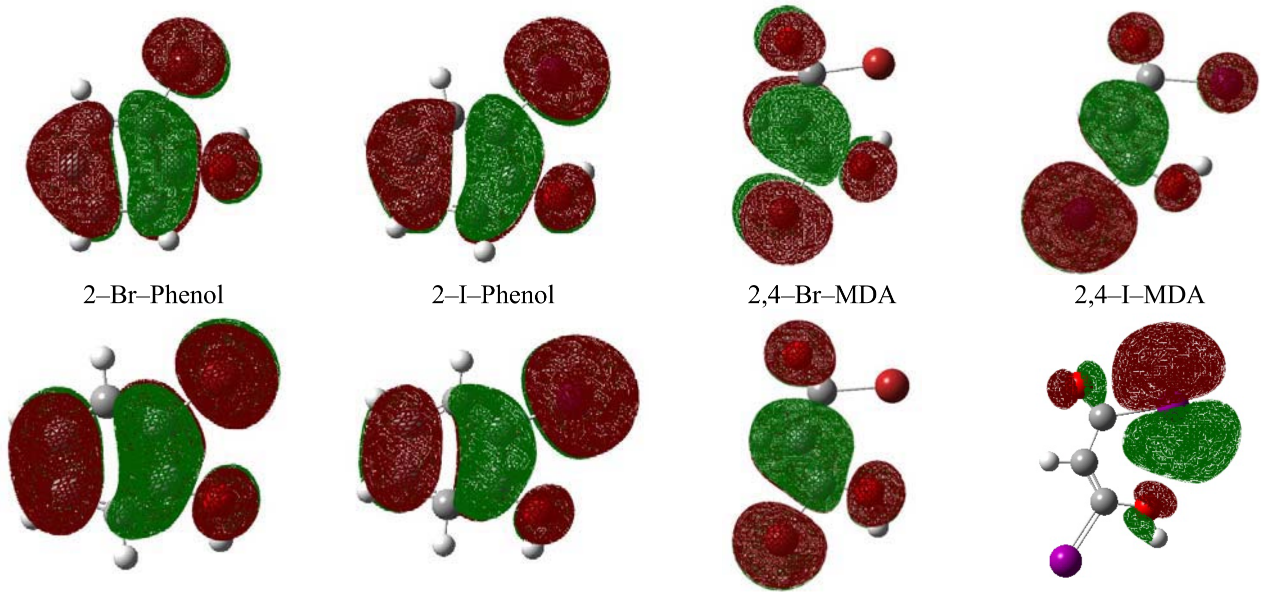

2–Br–Phenol 2–I–Phenol 2,4–Br–MDA 2,4–I–MDA

Figure 6. HOMO surfaces (HF/3–21G* results) of 2–Br–phenol, 2–I–phenol, 2,4–dibromo–malonaldehyde and 2,4–diiodo–malonaldehyde. Top: chelate conformations; bottom: open conformations.

6 CONCLUSIONS

Analysis of the obtained results allows to points out the following conclusions:

(*a*) The OH stretching mode anharmonic frequencies calculated at B3LYP/6–31G** and B3LYP/6–311++G(d,p) levels fit very well the experimental findings without using any scale factor.

(*b*) The disagreement concerning the trend of E_{HB} with electronegativity seems to be bound to the basis set extension, since the ring opening energies calculated with the less extended bases show a trend opposite to those calculated with more extended bases.

(*c*) Ovearll, if the simplest basis sets are ruled out, E_{HB} correlates with the OH frequency shifts better than with the electronegativity of the halogens series.

(*d*) The calculated E_{HB} values agree with the experimental estimates deduced from the temperature dependence of the infrared OH stretching band intensities better than with those estimated from the far IR OH rotational frequencies.

(*e*) The HOMO of the *open* conformers of 2,4–Br–MDA and 2,4–I–MDA is predicted to have *n*–character.

Acknowledgment

The author acknowledges the financial of this research by the University of Catania and by the Italian Ministero dell'Università e della Ricerca (MIUR), Roma.

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