

Study of the *Cis* and *Trans* Conformers of 2-Halophenols Using Coherent Anti-Stokes Raman Spectroscopic and Quantum Chemical Methods

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The OH stretching wavenumbers of the *cis* and *trans* conformers of 2-halophenols were studied in the gas phase by using coherent anti-Stokes Raman spectroscopy and quantum chemical calculations. The wavenumber differences between the two isomers of 2-fluoro-, 2-chloro- and 2-bromophenol were found to be 20, 71 and 102 cm⁻¹, respectively. These results are in good agreement with quantum chemical calculations based on the use of the density function theory. However, the calculated energy differences between two isomers decrease in the order Cl > Br > F. These results indicate that the vibrational wavenumber shift is not directly correlated with the strength of the intramolecular hydrogen bonding in 2-halophenols. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Although the hydrogen bond is a generally weak (10–50 kJ mol⁻¹) chemical bond, the importance and interest in it is based on its central role in a wide range of chemical and biochemical reactions.^{1–3} In these systems, hydrogen bonding is responsible for both intra- and intermolecular phenomena. Particular attention has been focused on the bond strength, geometry and stabilization energy induced by this bonding.

Hydrogen bonding involving phenol and its derivatives has been the subject of extensive theoretical^{4–6} and experimental^{7–20} studies as prototypes for the interaction of larger species. The simplest phenol derivatives, 2-halophenols,^{15–20} exhibit intramolecular hydrogen bonding in their conformational isomers, where there are two possible structures, i.e. *cis* and *trans* isomers, as shown in Fig. 1. The configuration of these two conformational isomers has been confirmed from the differences in the OH stretching^{15,16} and torsional¹⁷ wavenumbers between these two isomers since these wavenumbers are affected by hydrogen bonding. The experimental results have suggested that the *cis* isomer is more stable than the *trans* isomer. This suggestion is also supported by an *ab initio* molecular orbital (MO) study at the HF/6–31G level in 2-fluorophenol.⁴ However, there is a large difference in the experimental values of the magnitude of the hydrogen bonding strength between these two isomers. In addition, an MO

study on 2-fluorophenol found a large discrepancy from the experimental value for the energy difference between the two isomers⁴ and, unlike 2-fluorophenol, the geometries and energetics of 2-chloro- and 2-bromophenol have not yet been studied by quantum chemical methods.

The present study aimed to investigate the presence of and changes in the OH stretching wavenumbers of the *cis* and *trans* isomers in the gas phase as a function of the halogen atom of 2-halophenols, i.e. 2-fluoro-, 2-chloro- and 2-bromophenol. We investigated the OH wavenumber shift due to the hydrogen bonding using coherent anti-Stokes Raman spectroscopy (CARS)^{21,22} and discuss whether the shifts in the stretching wavenumbers can be correlated with the hydrogen bonding strengths in 2-halophenols. Quantum chemical calculations using the density function method (DFT) were also performed to provide additional information concerning the molecular structures, energies and the OH

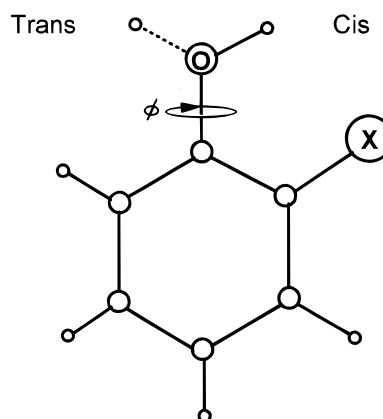


Figure 1. Structure of *cis* and *trans* isomers of 2-halophenols (X = F, Cl and Br).

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stretching wavenumbers of the two isomers of 2-halophenols.

EXPERIMENTAL

The CARS spectra of 2-halophenols in the gas phase were obtained using a CARS spectrometer, which has been described in detail elsewhere.^{23–25} The set-up consists of a frequency-doubled Nd:YAG laser (Quantel YG661-10) producing the pump beam and an Nd:YAG pumped dye laser (Lumonics Hyper SLM) producing the Stokes beam. Typical pulse energies and bandwidths were *ca.* 4 mJ and *ca.* 100 MHz for the pump beam and *ca.* 7 mJ and *ca.* 500 MHz for the Stokes beam, and the pulse width was 3–5 ns. The laser beams were adjusted to obtain the optimum spatial and temporal overlap. The laser beams were directed to a cylindrical stainless-steel static sample cell of diameter 7 cm and length 15 cm. The laser beams were focused on to the center of the sample cell by an $f = 250$ mm lens and the beams emerging from the sample cell were then collimated using another $f = 250$ mm lens. The CARS signal, separated from the pump and Stokes beams by a Pellin–Broca prism, was then transferred through an iris which blocked the remaining pump and Stokes beams and focused on to a 600 μm diameter optical fiber. The signal was further filtered by a 1 m monochromator (Jobin-Yvon THR1000) and was then detected by a photomultiplier (Hamamatsu R955) coupled with a boxcar averager (SR250). Data acquisition was performed using a personal computer (IBM 386 compatible) interfaced with the boxcar averager.

2-Fluorophenol (Aldrich Chemical, 98%), 2-chlorophenol (Junsei Chemical, 99%) and 2-bromophenol (Aldrich Chemical, 98%) were used after purification through both distillation and vacuum sublimation in a series of freeze–pump–thaw cycles. Experiments were typically performed at pressures below 25 Torr and in the temperature range 300–358 K.

RESULTS

CARS measurements

The red shift of the hydrogen-bonded OH stretching wavenumber, $\tilde{\nu}_{\text{OH}}$, and the blue shift of the hydrogen-bonded OH torsional (out-of-plane) wavenumber, $\tilde{\nu}_{\text{OHX}}$, may be used as indicators for the formation of hydrogen bonds in 2-halophenols. Although the torsional wavenumber of 2-halophenols involves O and H atoms in addition to the remaining atoms, $\tilde{\nu}_{\text{OH}}$ is localized only on O and H atoms. Therefore, we measured $\tilde{\nu}_{\text{OH}}$ in 2-halophenols to characterize the conformation and ascertain whether the shift of $\tilde{\nu}_{\text{OH}}$ can be correlated with the hydrogen bond strength.

The CARS signals of the OH stretching wavenumbers for 2-fluorophenol (2FP), 2-chlorophenol and 2-bromophenol (2BP) are shown in Fig. 2(a), (b) and (c), respectively. In the region between 3500 and 3680 cm^{-1} , a pair of vibrational bands was assigned to OH stretching wavenumbers of the *cis* and *trans* isomers.

No other peaks were observed beyond this wavenumber region since the nearest possible peak, i.e. CH stretching, is a few hundred cm^{-1} away.

The vibrational bands of 2-halophenols are complicated for two reasons: the existence of two rotational isomers and the presence of a large number of rotational transitions at the elevated temperature of the static sample cell. Since the intramolecular hydrogen bonding of the *cis* isomer is expected to reduce the force constant of the OH functional group, the vibrational band of the lower wavenumbers is assigned to the *cis* isomer in the CARS spectra of the 2-halophenols. On the other hand, that of the higher wavenumbers close to the OH stretching (3657 cm^{-1}) of phenol⁹ is assigned to the OH stretching of the *trans* conformer.

Table 1 summarizes the observed and calculated OH stretching wavenumbers of the *cis* and *trans* isomers for 2-halophenol molecules. For the halogen substituents of 2-halophenols from fluorine to bromine, the OH stretching wavenumber of the *trans* isomers remains unchanged in the vicinity of *ca.* 3656 cm^{-1} , whereas that of the *cis* isomers decreases gradually from 3636 cm^{-1} for 2FP to 3584 cm^{-1} for 2CP and to 3556 cm^{-1} for 2BP (these values were obtained at the mid-point of each vibrational band in the CARS spectra in Fig. 2). The most recent values for the OH stretching vibration obtained by non-resonant ionization detected IR spectroscopy (NID-IR) have been assigned tentatively to 3634 cm^{-1} for *cis* and 3662 cm^{-1} for *trans*.¹⁶ Considering the *ca.* 10 cm^{-1} spread of the observed bandwidth in the cited experiments on jet-cooled 2FP,¹⁶ our result is in good agreement with that of NID-IR. With regard to the results of Lin and Fishman,¹⁵ although $\tilde{\nu}_{\text{OH}}$ of the *trans* isomer is about 10 cm^{-1} lower than our results, $\tilde{\nu}_{\text{OH}}$ of the *cis* isomer is in good agreement with our results.

Since the intensity of the CARS signal is proportional to the square of the third-order non-linear susceptibility $\chi_{\text{CARS}}^{(3)}$ of the molecule and $\chi_{\text{CARS}}^{(3)}$ is proportional to the number density of molecule N , it is generally written that the CARS signal scales quadratically with the number density of molecules.²² With regard to the present experiments, the square root of the OH stretching vibrational intensity ratios of two isomers correlates directly with the number densities of the two isomers. In Fig. 2, the observed intensities of the *cis* isomers are much higher than those of the *trans* isomers in 2-halophenols, indicating that the *cis* isomer is more stable than the *trans* isomer.

Computational results

The quantum chemical calculations on 2-halophenols were carried out according to the density functional method (DFT) using the Gaussian 94 program.²⁶ We employed the Becke3LYP method, which includes the B3 exchange corrections in combination with the Lee–Yang–Parr correlation correction.²⁷

The DFT method was performed to obtain the full geometry optimization, harmonic wavenumbers and energies of the 2-halophenols, utilizing the 6–31G(d,p) basis set for 2FP and 2CP and 6–311G(d,p) for 2BP. Some selected values for the *cis* and *trans* isomers, both with C_s symmetry point groups, are listed in Table 2. It can be seen that there is no marked structural effect

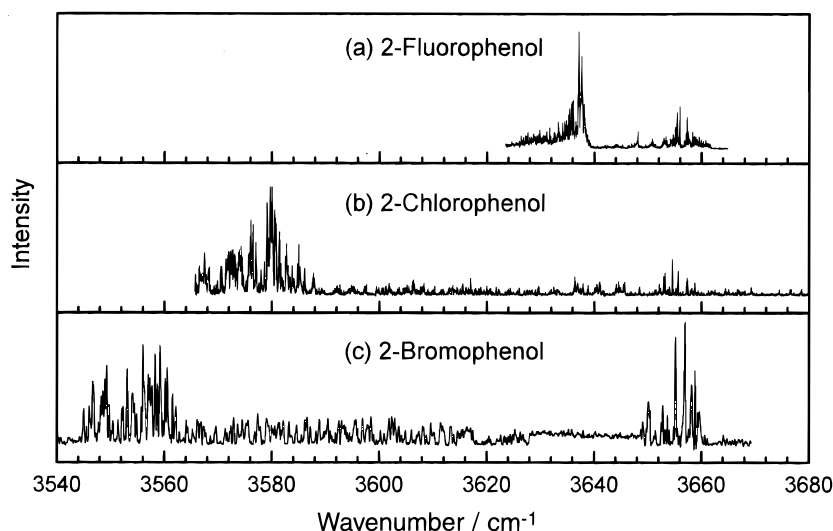


Figure 2. Observed CARS spectra of the OH stretching region in the gas phase of 2-halophenols. The experimental conditions were $P = 22$ Torr and $T = 353$ K for 2-fluorophenol (a), $P = 12$ Torr and $T = 353$ K for 2-chlorophenol (b) and $P = 12$ Torr and $T = 333$ K for 2-bromophenol (c).

ascribed to intramolecular hydrogen bond formation. The calculated hydrogen bond distances are $R(\text{H} \cdots \text{X})_{2\text{FP}} = 2.178$, $R_{2\text{CP}} = 2.417$ and $R_{2\text{BP}} = 2.468$ Å. The hydrogen bond angle, $\angle \text{OHX}$, is about 10° smaller in 2FP than 2CP and 2BP. This geometric information has not been reported for all the 2-halophenols but values for 2FP are available from a gas-phase electron diffraction study.¹⁹ The reported values of the hydrogen bond length $R(\text{H} \cdots \text{F})$ and angle $\angle \text{OHX}$ for 2FP are 2.13 ± 0.05 Å and $120.8 \pm 4.5^\circ$, respectively. This is in good agreement with our values calculated by the DFT.

DISCUSSION

The OH stretching and OH torsional wavenumbers are very sensitive to hydrogen bonding. As shown in Table 1, there are major changes in two wavenumbers, $\tilde{\nu}_{\text{OH}}$ and $\tilde{\nu}_{\text{OHX}}$. The stretching mode, $\tilde{\nu}_{\text{OH}}$, is red shifted owing to the reduction of the force constant of the OH bond and the torsional mode, $\tilde{\nu}_{\text{OHX}}$, the blue shifted because the ability of the OH group undergoes torsion

Table 1. Comparison of the observed and calculated OH stretching ($\tilde{\nu}_{\text{OH}}$) and torsional ($\tilde{\nu}_{\text{OHX}}$) wavenumbers for 2-halophenols

Compound		This work			Ref. 15	Ref. 16	Ref. 17
		$\tilde{\nu}_{\text{OH}}^{\text{exp}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{OH}}^{\text{cal}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{OHX}}^{\text{cal}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{OH}}^{\text{exp}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{OH}}^{\text{exp}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{OHX}}^{\text{exp}}/\text{cm}^{-1}$
2FP	<i>cis</i>	3636	3791	430	3635	3634	379
	<i>trans</i>	3656	3825	336	—	3662	342
2CP	<i>cis</i>	3584	3760	417	3583	—	407
	<i>trans</i>	3655	3824	319	3645	—	373
2BP	<i>cis</i>	3554	3738	436	3562	—	404
	<i>trans</i>	3656	3830	343	3646	—	372
2IP	<i>cis</i>	—	—	—	3538	—	386
	<i>trans</i>	—	—	—	3647	—	357

^a The values presented were obtained from the mid-point of each vibrational band in the CARS spectra in Fig. 2.

^b Not scaled by a factor of 0.963 for the values calculated using B3YLP/6–31G(d,p) or 6–311G(d,p).

Table 2. Selected equilibrium parameters, energies and zero-point vibrational energies

Compound		$R(\text{OH})/\text{\AA}$	$R(\text{HX})^{\text{a}}/\text{\AA}$	$R(\text{XC})/\text{\AA}$	$\angle \text{OHX}^{\text{c}}$	Energies ^b /hartree	ZPVE ^c /kJ mol ⁻¹
2FP	<i>cis</i>	0.969	2.178	1.364	113.2	-406.709683	254.312
	<i>trans</i>	0.966	—	1.348	—	-406.704679	253.534
2CP	<i>cis</i>	0.970	2.417	1.767	119.6	-767.074708	250.697
	<i>trans</i>	0.966	—	1.753	—	-767.069118	249.446
2BP	<i>cis</i>	0.968	2.486	1.927	122.8	-2881.096528	248.115
	<i>trans</i>	0.963	—	1.913	—	-2881.091359	247.521

^a Bond distance $R(\text{HX})$ between hydrogen atom of OH group and halogen atom.

^b Absolute energies calculated using the 6–31G(d,p) basis set for 2FP and 2CP and the 6–311G(d,p) basis set for BP.

^c Zero-point vibrational energy [not scaled by a factor of 0.963 for the value calculated using B3YLP/6–31G(d,p) or 6–311G(d,p)].

is strongly restricted by hydrogen bonding to the halogen atoms.

Among various proposed calculations, B3LYP is usually found to be fairly reliable in predicting the fundamental wavenumber.^{28,29} The $\tilde{\nu}_{\text{OH}}$ and $\Delta\tilde{\nu}_{\text{OH}}$ obtained from DFT calculations are also in good agreement with the observed values, considering that there is a scaling factor of 0.963 for B3LYP/6-31G(d) and 6-31G(d,p).³⁰ However, considerable disagreement between the observed and calculated values is found for the torsional wavenumber. For 2-halophenols, DFT calculation underestimates $\tilde{\nu}_{\text{OHX}}$ of the *trans* isomer, whereas it overestimates $\tilde{\nu}_{\text{OHX}}$ of the *cis* isomer. This result gives rise to a large discrepancy between the calculated and observed values in $\Delta\tilde{\nu}_{\text{OHX}}$.

The greater stability of the *cis* over the *trans* form has already been demonstrated for 2-halophenols both theoretically⁴ and experimentally.^{15,17} However, there are great differences in the order and magnitude of the hydrogen bonding strength in 2-halophenols according to the experimental and calculation methods, as shown in Table 3. In earlier work, Lin and Fishman¹⁵ measured the relative intensities of *cis* and *trans* isomers as a function of temperature and obtained energy differences of 14.27, 13.10 and 11.51 kJ mol⁻¹ for 2CP, 2BP and 2IP, respectively. Later, Carlson *et al.*¹⁷ calculated the energy difference between *cis* and *trans* isomers from the OH torsional wavenumber values observed by far-IR spectroscopy. These energy differences are much smaller than those of Lin and Fishman,¹⁵ as shown in Table 3. On the other hand, George *et al.*⁴ reported the energy difference of 2FP to be 16.99 kJ mol⁻¹ calculated at the HF/6-31G level. This is much larger than the experimental value of 6.82 kJ mol⁻¹. The present study with DFT gives 12.68 kJ mol⁻¹ for 2FP, 13.68 kJ mol⁻¹ for CP and 13.31 kJ mol⁻¹ for 2BP after thermal energy correction at 298.15K. Although the difference between our and Carlson *et al.*'s values for the stabilization energy is small in comparison with the previously calculated result, there are still considerable differences in both the magnitude and the direction of hydrogen bonding between the theoretical and experimental values. The experimental value is also uncertain owing to the use of only two terms in a cosine series and the considerable overlap between the bands of the two isomers in the analysis of the experimental data. As shown in Table 3, the relative order or hydrogen bonding strength is F = Cl > Br > I in Carlson *et al.*'s experiment and Cl > Br > F in our DFT. The results indicate that further higher calculations and precise experiments are needed to gain the information on the hydrogen bonding strength in 2-halophenols.

Table 3. Energy differences (ΔE) between *cis* and *trans* isomers

Compound	This work ^a	$\Delta E/\text{kJ mol}^{-1}$		
		Ref. 4	Ref. 17	Ref. 16
2FP	13.14 (12.68)	16.99	6.82	—
2CP	14.69 (13.68)	—	6.82	14.27
2BP	13.56 (13.31)	—	6.40	13.10
2IP	—	—	5.52	11.51

^a Absolute energy differences calculated from the quantum chemical calculation (with inclusion of the thermal energy correction at 298.15K in parentheses).

The shift in $\Delta\tilde{\nu}_{\text{OH}}$ for 2-halophenols increases with the size of the halogen atom, but the calculated and experimental energy differences between the two isomers give different orders. Therefore, the experimental and theoretical results occur in outlining that, although the $\Delta\tilde{\nu}_{\text{OH}}$ shift is a measure of the interaction between the OH and halogen atoms in 2-halophenols, it is not a measure of the strength of the hydrogen bond. Hartland *et al.*³¹ also did not find a direct correlation between the vibrational wavenumber shifts and relative energies in their study of phenol and solvent complexes.

Although fluorine is more electronegative than Cl and Br and the hydrogen bond distance $R(\text{H}\cdots\text{X})$ is shorter in 2FP than in 2CP and 2BP, the stabilization energy of 2FP is smaller than those of 2CP and 2BP derived from the absolute total energies in Table 2. The trend in the strengths of the hydrogen bond indicates that the hydrogen bond of 2FP is weaker than those of 2CP and 2BP. Considering that the van der Waals radii of HF, HCl and HBr molecules are 2.55, 3.0 and 3.15 Å, respectively, we know that the bond distances of $R(\text{H}\cdots\text{X})$ for the *cis* isomers of 2-halophenols are much smaller than their corresponding van der Waals radii. The corresponding bond length differences between the hydrogen bond length $R(\text{H}\cdots\text{X})$ and the van der Waals radius $R(\text{HX})$ are 0.372, 0.583 and 0.664 Å for 2FP, 2CP and 2BP, respectively. Therefore, the small size of the fluorine atom prevents the OH group from approaching close enough for strong bonding. For example, the bond length in 2FP $R(\text{H}\cdots\text{X}) = 2.178$ Å, is much longer than the 1.9 Å $\text{HF}\cdots\text{HF}$ bond distance in $(\text{HF})_2$.³² Despite the larger overlap between H and Br atoms in 2BP, however, the stabilization energy is lower than that of 2CP. This indicates that a balance between the optimum interacting distance and minimum repulsion is formed in 2CP. These results may explain why the stabilization energies of 2CP and 2BP are larger than that of 2FP.

CONCLUSIONS

We have carried out CARS and quantum chemical studies on 2-halophenols. Although the OH stretching wavenumber shift was increased as the substituent of the 2-halophenols varied from fluorine to bromine, the strength of the intrahydrogen bonding obtained by using quantum chemical calculation with DFT decreased in order Cl > Br > F. These results indicate that the vibrational wavenumber shift is not directly correlated with the strength of the intramolecular hydrogen bonding in 2-halophenols.

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