Intramolecular Chelation of Chlorinated 2-Phenoxyphenols

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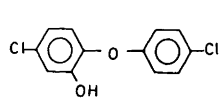
The structures of the hydrogen-bonded, monomeric structures of chlorinated 2-phenoxyphenols have been re-examined. IR measurements indicate that intramolecular OH··O and OH··Cl bonds are prevalent. *ortho* Chloro substitution leads to twisted conformations, an interpretation which is supported by ^{1}H NMR chemical shift data.

In an earlier study of chlorinated 2-phenoxyphenols,[1] we concluded that intramolecular hydrogen-bonding effects on ^{13}C NMR shieldings were minor compared to shielding variations caused by steric perturbations.



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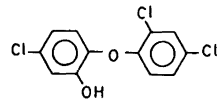

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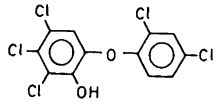

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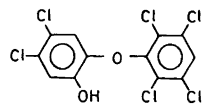

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IR absorptions of compounds **1–4** were interpreted as being dependent on the intramolecular OH··π hydrogen bond. This interpretation was based on previously published data by Kovac *et al.*[2] From an IR study of bis(*o*-hydroxyphenyl) alkanes and sulfides they concluded that these compounds exist predominantly as OH··π and OH··O hydrogen-bonded conformers.

Intramolecular OH··π interactions were recognized early in similar compounds, such as 2-hydroxydiphenylmethanes.[3] This system has subsequently been investigated[4] using IR spectroscopy, where it was found that the energy of the OH··π hydrogen bond increased with increase in the number of alkyl groups on the benzyl moiety. Furthermore, it has been reported that the strong OH··π interaction persists even in the solid state.[5]

In a paper on ^{1}H NMR measurements on *o*-substituted phenols in $CDCl_3$,[6] the results for 2-hydroxydiphenylmethane were interpreted in terms of intermolecular OH··O as well as intramolecular OH··π hydrogen-bonding. However, this study[6] offered no explanation for the results obtained for 2-phenoxyphenol and 2-hydroxydiphenyl sulfide. In another study, the single absorption observed for 2-phenoxyphenol in CCl_4 (ν_{OH} = 3562 cm^{-1}) was assigned to the intramolecular OH··O hydrogen bond.[7]

The assignment of the OH··π interaction of bis (2-hydroxy-3-*t*-butyl-5-methylphenyl) sulfide[2] has recently been criticized by Schaefer *et al.*[8] They claim, from measurements of ^{1}H NMR parameters, that the most favourable conformation involves two intramolecular OH··S bonds, yielding a twisted conformation. In the same study, the ^{1}H NMR spectrum of 2-hydroxydiphenyl sulfide was analyzed and it was concluded that the phenyl group lies roughly perpendicular to the substituted benzene plane (skew conformation) including an intramolecular OH··S hydrogen bond and with the sulfur orbitals in conjugation with the phenyl π system.

We have made a similar observation with 2-phenoxyphenols[1] and also with diphenyl ethers,[9] in which the *ortho* substitution on one ring causes a shielding of the *ortho* and *para* positions of the other ring. Furthermore, from studies of 2-hydroxyanisole[10] and 2-hydroxythioanisole,[8] it is recognized that the former has a planar con-

formation. In contrast, in the thioanisole compound the S–CH_3 bond is perpendicular to the aromatic ring plane. In addition, there are intramolecular OH··O and OH··S hydrogen bonds in these structures.

Experimental

The chlorinated 2-phenoxyphenols **2** and **4** were a generous gift from Ciba-Geigy. Compounds **1** and **3** were prepared according to Nilsson.[11]

Chloroform-*d* (99.8 % ^2H) which had been distilled over P_2O_5 and stored over 4 Å molecular sieves was used as solvent for the ^1H NMR measurements. Carbon tetrachloride was distilled and stored over 4 Å molecular sieves before use in the IR experiments.

The ^1H NMR spectra were recorded on a JEOL C60-HL spectrometer operating in the CW mode. The chemical shifts were measured at 26 °C using TMS as internal standard.

The IR measurements were performed on a Perkin-Elmer 681 instrument. The spectrometer was purged with Ar and 6.0 cm variable cells fitted with NaCl windows were used, both for the sample and for the solvent reference.

Results and discussion

In view of the results mentioned above, and since our conclusions concerning the OH··π interaction in the chlorinated 2-phenoxyphenol system were based mainly on the recently criticized work of Kovac *et al.*,[2] we made some additional IR measurements on compounds **1–4** (Table 1). Using lower concentrations and with improved instrumental resolution, we were able to resolve the single absorption into two bands (Fig. 1; compounds **2, 3** and **4**). Both bands appear in the intramolecular hydrogen-bonding region, and the bands at lower wavenumber are somewhat broader, indicating a greater molecular flexibility. These bands could be due to OH··Cl interactions. Thus, our IR data indicate that there are several intramolecular hydrogen bonds. The first absorption band is assigned to OH··O (or OH··Cl) and appears at 3585–3587 cm^{-1} for **1, 2, 3** and **4**. The second absorption band for **2, 3** and **4** is assigned to OH··Cl stretching. This indicates that the OH group in **2** and **4** interacts with a chlorine on the other ring. In compound **3**, the OH group may be involved in interactions with

Table 1. IR hydroxy absorptions of compounds **1–4** at 0.1 mM in CCl_4.

Compd.	$\nu_{OH\cdot O}/cm^{-1}$	$\nu_{OH\cdot Cl}/cm^{-1}$
1	3586	–
2	3587	3563
3	3586	3542
4	3585	3567

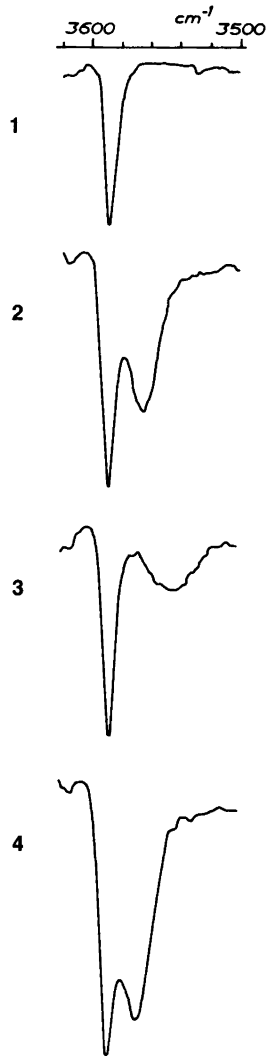

Fig. 1. IR hydroxy absorptions of compounds **1–4**.

Table 2. ^{1}H NMR chemical shifts for the most shielded protons (H-3) and the OH protons of compounds **1–4** at 0.010 M in $CDCl_3$.

Compd.	$\delta_{H\text{-}3}$/ppm	$\delta_{OH\text{-}3}$/ppm
1	6.69	5.46
2	6.63	5.53
3	6.67	5.85
4	6.35	5.59

an *ortho* chlorine on the phenol ring as well as with a chlorine atom on the other ring. Consequently, the single band that appears for **1** is assigned to the intramolecular OH··O (or OH··π) absorption.

The hydroxy ^{1}H NMR chemical shift for 2-hydroxy-5-chlorodiphenylmethane appears at 4.43 ppm,[12] where the signal for OH involved in an intramolecular interaction is known to occur. This signal is high-field shifted by more than 1 ppm relative to the chlorinated 2-phenoxyphenols (Table 2), the shift presumably being due, in part, to the magnetic anisotropy of the phenyl group. In addition, the O*H* signal (CCl_4) for 2-hydroxyanisole appears at 5.41 ppm.[10] In other words, δ_{OH} for **1, 2, 3** and **4** does not suggest a direct OH··π interaction, assuming that the interaction is symmetrical, i.e. that the proton is situated in the direction of the symmetry axis of the benzene plane.[13] Furthermore, the magnitude of δ_{OH} indicates that a twisted conformation is predominant, where O–*H* is coplanar with the ring and is involved in equilibrium interactions with the ethereal oxygen and a chlorine (whether *ortho* on the phenol ring or *ortho* on the other ring) (Fig. 2). Conformations in which which an OH··π interaction could occur are believed to be of minor importance. Comparison of the ^{1}H NMR signals for the most shielded aromatic protons in **1, 2, 3** and **4** (H-3 protons on the phenolic rings) reveals a significant shielding effect in **4**, in accordance with a more twisted skew conformation with the H-3 proton in the shielding region of the other ring. This observation is in accordance with results obtained in conformational studies of tri-*ortho* substituted diphenylmethanes[14] and diphenyl ethers[15].

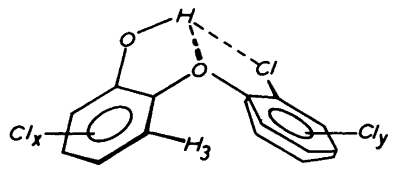

Fig. 2. Monomeric structure of chlorinated 2-phenoxyphenols where the intramolecular hydrogen bond is either OH···O or OH···Cl.

In conclusion, shieldings of carbons in chlorinated 2-phenoxyphenols are mainly determined by conformational preferences due to *ortho* substitution, thus attaching only minor importance to intramolecular hydrogen-bonding effects[1]. *Ortho* substitution on one ring causes a shielding of *ortho* and *para* positions of the other ring, i.e. twists the *ortho*-substituted ring out of the conjugation plane and increases the *p*-π-*p*-π interaction with the other aryl moiety. Monomeric structures involve intramolecular hydrogen-bonding, where the intramolecular OH··O and OH··Cl hydrogen bonds yield predominantly a twisted conformation[16].

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