Torsional Barriers in *para*-Substituted Phenols from *ab initio* Molecular Orbital Theory and Far Infrared Spectroscopy

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Summary The effects of *para* substituents (OH, F, Me, CHO, CN, and NO_2) on the barrier to rotation about the C–O bond in phenol as determined by *ab initio* molecular orbital calculations and far i.r. spectroscopic measurements are generally in close agreement; substituents which are π-electron donors lower the observed barrier while π-electron acceptors raise the barrier.

BOTH theory[1] and experiment[2] predict that phenol is planar. A planar structure is stabilized by delocalization of the *p*-type lone pair on oxygen [structure (I)]; this is likely to be more effective than the delocalization of the more tightly bound sp^2-type lone pair in the orthogonal form (II). The energy difference represents the barrier to rotation about the C–O bond. This barrier is considerably larger than in aliphatic alcohols reflecting, in part, the increased double bond character in the C–O bond.

Campagnaro, Hall, and Wood[3] examined far i.r. spectra of several *para*-substituted phenols and observed changes in the OH torsional frequency which they correlated with the qualitative electronic properties of the substituent.† To confirm and extend these ideas, we have carried out *ab initio* molecular orbital calculations and far i.r. spectroscopic measurements of the torsional barriers in the *para*-substituted phenols XC_6H_4OH (X = OH, F, Me, H, CHO, CN, and NO_2).

Far i.r. spectra of the phenols in cyclohexane solution (*ca.* 0·01M) were obtained by procedures described elsewhere.[4] The far i.r. spectra of the analogous deuteriated phenols were also obtained to confirm the assignments of the torsional frequencies.[4] The MO–LCAO approximation[5] was used with the STO-3G basis set[6] and standard geometries.[7] Orbital and overlap electron populations are calculated using Mulliken's method.[8]

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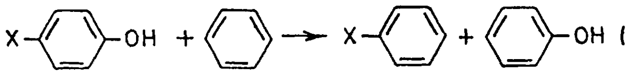
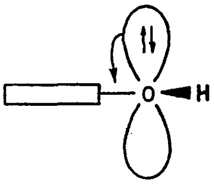
† Other spectroscopic studies of the effects of *para*-substituents have been reported for benzaldehydes[3] and anilines (D. G. Lister and J. K. Tyler, *Chem. Comm.*, 1966, 152; A. Hastie, D. G. Lister, R. L. McNeil, and J. K. Tyler, *Chem. Comm.*, 1970, 108).

Results are quoted in the Table where the quantities listed have the following meanings. ΔV_2 is the change‡ in the twofold barrier from the value in phenol, $q_\pi(X)$ is the π charge on the substituent X (a positive value indicates that X is a π donor), Δq_π (OH) is the change in π charge on OH relative to the value in phenol, and $\Delta\pi_{C-O}$ is the corresponding change in the double bond character of the C–O bond as measured by the π-overlap population. The interaction energy of the substituent X with the OH group in para position to it is measured by the energy change in the formal reaction (1). If X and OH do not interact, the energy change in (1) would be zero. Interaction energies are listed for both planar and orthogonal orientations of the OH group in (1).


(1)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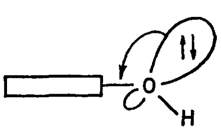
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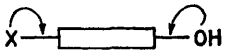
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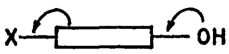
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Calculated and experimental quantities for para-*substituted phenols*

X	ΔV_2 (kcal mol^{-1}) Exp.	Calc.	$q_\pi(X)^a$	$\Delta q_\pi(OH)^a$	$\Delta\pi_{C-O}^a$	Interaction energy (kcal mol^{-1}) Planar	Orthogonal
OH	−0·87	−0·95	+0·096	−0·006	−0·006	−1·4	−0·5
F	−0·60	−0·53	+0·074	−0·002	−0·003	−0·9	−0·4
CH_3	−0·32	−0·28	+0·008	−0·002	−0·002	−0·4	−0·1
H	0	0	0	0	0	0	0
CHO	+0·87	+0·47	−0·041	+0·006	+0·004	+0·7	+0·2
CN	+0·70	+0·66	+0·029	−0·009	+0·006	+0·8	+0·2
NO_2	+0·98	+1·02	−0·039	+0·013	+0·009	+1·3	+0·3

[a] Values quoted for planar conformations.

[b] Twofold (V_2) component of barrier calculated *via* a two term Fourier expansion:

$$V(\phi) = V_1\,(1 - \cos\phi)/2 + V_2\,(1 - \cos 2\phi)/2$$

The most stable conformation when X = OH has HO ··· OH *trans* and the *cis–trans* energy difference is 0·07 kcal mol^{-1}. The most stable conformation when X = CHO has HO ··· CO *cis* and the *cis–trans* energy difference is 0·08 kcal mol^{-1}.

The table shows: (1) Although the calculated barrier in phenol (5·16 kcal mol^{-1})[1] is considerably higher than the experimental value (3·56 kcal mol^{-1}), the changes in barrier with substitution as shown in Table I are generally in close agreement. (2) The barrier is found to decrease when X is a π-electron donor [positive $q_\pi(X)$ charges] and conversely. (3) These results are easily rationalized in terms of the opposition (III) to, or reinforcement (IV) of, delocalization of the oxygen lone pair electrons by the substituent X. Thus, when X is a π-donor (III), π-electron donation by OH decreases [Δq_π(OH) is negative], the double bond character in the C–O bond decreases [$\Delta\pi_{C-O}$ is negative] and the barrier decreases. Conversely, when X is a π-acceptor (IV), electron donation by OH increases, the double bond character in the C–O bond increases and the barrier increases. The theory thus confirms the conclusions reached by Campagnaro, Hall, and Wood.[3] (4) The calculated values of the interaction energies show that when X is a π-donor, the interaction between X and OH is destabilizing (negative interaction energies) and the converse also holds. This is true in both planar and orthogonal conformations although smaller in the latter. There is an almost linear correlation between the barrier values and the interaction energies in the planar forms.

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‡ In all cases we take the *change* in a calculated or experimental quantity to be the value in the substituted phenol less the value in phenol.

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