

ESTIMATION OF THE OH...O INTERACTION ENERGY IN INTRAMOLECULAR HYDROGEN BONDS: A COMPARATIVE STUDY

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An empirical formula relating directly H...O interatomic distance to H...O interaction energy is used to estimate this energy in intramolecular O—H...O hydrogen bonds calculated for systems of known precise geometry. The values obtained were correlated with spectroscopic characteristics of the H-bond ($\Delta\nu$ for OH bands in IR spectra and NMR chemical shifts, δ , for protons) and CNDO and INDO estimations of H-bond energy. The regressions obtained had good or very good correlation coefficients.

INTRODUCTION

There is a simple but fundamental difference between inter- and intramolecular hydrogen bonding: in the latter it is impossible to define the hydrogen bond energy uniquely.^{1,2} There is always some additional conformational and/or electronic or steric contribution to the energy which changes on passing from the reference state to the H-bound state. The experimentally determined enthalpy difference between a conformer with a free OH group and with any intramolecularly H-bonded OH group (OH...O) always contains some contribution of conformational energy and hence cannot be a reliable measure of hydrogen bond energy. Various theoretical approaches have been made to solve these problems. Several different definitions and procedures for calculating intramolecular H-bond energy have been proposed,¹⁻⁵ but none of them was completely successful. The stretching frequency shift in IR spectra, $\Delta\nu$, is widely used as a probe of H-bond strength. Owing to the inaccessibility of reliable experimental values for the intramolecular H-bond energy, the correlation between the energy and IR shift $\Delta\nu$, known for several intermolecular H-bond types (the Badger-Baure rule), cannot be tested in this case. Another difference between the inter- and intramolecular H-bonds is that the latter are often bent. Hence the O...O interatomic

distance provides no reliable information about the strength of the H-bond.

To overcome the above-mentioned difficulties, we have attempted to estimate H-bond energies for molecular and ionic systems containing an O—H...O interacting system based on the experimentally determined H...O interatomic distance. In order to do this we applied an extrapolation equation (4) relating the energy of an H...O interaction directly with this interatomic distance.

ESTIMATION OF H...O INTERACTION ENERGY DIRECTLY FROM H...O INTERATOMIC DISTANCES

It has already been shown⁶ that by combining Pauling's⁷ bond number [equation (1)] with Johnston and Parr's⁸ empirical equation for bond energy [equation (2)] we obtain an effective extrapolation equation [equation (3)] enabling the O...H interaction energy to be estimated directly from the O...H interatomic distance:

$$d(n) = d(1) - c \ln n \quad (1)$$

$$E(n) = E(1)n^p \quad (2)$$

$$E(n) = E(1)\exp\{\alpha[d(1) - d(n)]\} \quad (3)$$

where $d(1)$ is a standard 'single bond' length for which the bond number $n = 1$, $d(n)$ is the bond length with bond number equal to n , $E(1)$ is the 'single bond' energy, $E(n)$ is the energy of the bond with bond number n and $\alpha = p/c$ and is determined empirically for each particular type of bond. In order to estimate α for O—H...O interactions, we chose (as previously⁶) the following data: $d(1)$ is the O—H bond length in a water molecule, equal to 0.957 Å,⁹ whereas for $d(n)$ we took the central H...O interatomic distance in the (H₂O.H.OH₂)⁺ complex,¹⁰ which is 1.22 Å. The bond energies are $E(1) = 468.9$ kJ mol⁻¹ (Ref. 11) and $E(n) = 150.0$ kJ mol⁻¹ (Ref. 12), respectively, and were determined for the same systems. In other words, $d(n)$ and $E(n)$ are given for the same n . The estimated value of α for these data is 4.338 Å⁻¹. Hence for the O...H interaction equation (3) becomes

$$E(n) = 468.9 \exp[4.338(0.957 - r_{\text{H}\cdots\text{O}})] \quad (4)$$

where $R_{\text{H}\cdots\text{O}}$ is the H...O interatomic distance in Å, i.e. $d(n)$ in equation (3).

In order to test the above model we used the geometries of a set of 28 intermolecular O—H...O systems determined by the neutron diffraction technique¹³ and also applied equation (4) and, for comparison, the Lippincott and Schroeder potential for H...O interactions, $V_{2,5}$,¹⁴ with parameterization optimized for O-H...O systems:¹⁵

$$E_{\text{L.-S.}} = V_2 = -D^* \exp[-n^*(R - r - r_0^*)^2/2(r - r_0)] \quad (5)$$

(the original notation from Ref. 14 is used), where D^* , n^* and r_0^* are parameters characterizing the O^{δ-}...H^{δ+} interactions and are related in a complex way to D , n and r_0 which apply to the O—H bond in a water molecule, r is the length of the O—H bond and R is the O...O distance in a dimer. Linear regression between $E(n)$ and $E_{\text{L.-S.}}$ for the above data gives

$$E[\text{equation (4)}] = 0.468E_{\text{L.-S.}} + 0.743 \text{ (in kJ mol}^{-1}\text{)} \quad (6)$$

with a correlation coefficient $r = 0.998$. The above qualitative agreement between the well accepted model of Lippincott and Schroeder and the results from equation (4) encouraged us to use this equation to estimate intramolecular H-bond energies.

RESULTS AND DISCUSSION

First, we have related the energy of H...O interaction calculated by use of equation (4) to the energy of O...H interaction calculated by use of the appropriate term [equation (5)] in the Lippincott-Schroeder potential, $E_{\text{L.-S.}}$,¹⁴ with the Derissen-Smit parameterization.¹⁵ As a sample for our study we chose 43 H-bonded systems with intramolecular H-bonds of the OH—O, OH⁺—O and (OHO)⁻ types of known precise

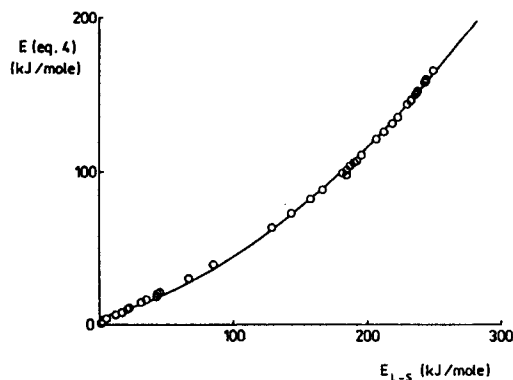


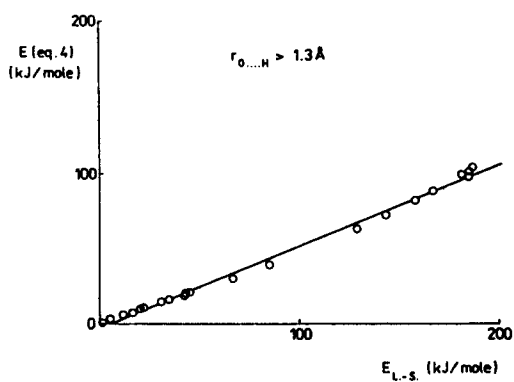
Figure 1. Scatter plot for dependence between O...H interaction energies estimated by use of equation (4) and using the respective Lippincott-Schroeder term [equation (6)] for all OH...O data

geometry.² Figure 1 presents the relationship, which is evidently curved. However, if the OH...O bonds are separated to form two subsamples, one consisting of weaker bonds for which $r(\text{O}\cdots\text{H}) > 1.3$ Å and the other consisting of stronger bonds for which $r(\text{O}\cdots\text{H}) < 1.3$ Å, then two linear regressions are obtained, as shown in Figure 2(a) and (b), with correlation coefficients $r = 0.997$ and 0.998 , respectively. The curvilinear dependence in Fig. 1 may result from non-linearity of the intramolecular bonds such as is typical in the case of intermolecular bonds. Hence the stronger contributions from repulsion may contribute in the case of intramolecular bonds. Equation 4 is an effective extrapolation equation which in principle contains all interactions, whereas equation (5) describes only H...O interactions.

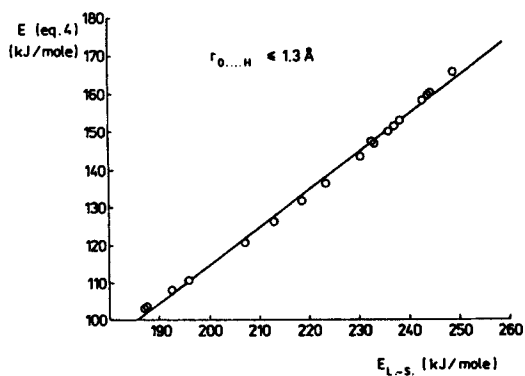
Another test for equation (4) may be based on spectral parameters describing H-bonds. Since $\Delta\nu_{\text{OH}}$ values in the infrared spectra and also δ_{H} values in the proton NMR spectra are often taken as being proportional to H-bonding energy,^{5,16,17} we plotted directly ΔE [equation (4)] against δ_{H} and $\Delta\nu_{\text{OH}}$, as shown in Figures 3 and 4. The data were taken from Refs 2 and 16 and are concerned with *ortho*-substituted phenols and other compounds with OH...O, (O...H⁺...O) and O...H...O⁻ intramolecular H-bonds for which the geometry was reliably determined.

The plot of δ_{H} vs E [equation (4)] is exceptionally good with a correlation coefficient of 0.983, indicating reliable equivalence between these two parameters. The other plot (Figure 4) seems to be poorer. This is readily understood in view of the fact that it is difficult to estimate precisely the frequency shift in the infrared spectra of the enolic forms of β -diketones and of compounds with very strong intramolecular H-bonds.^{2,16}

Finally, we carried out CNDO/2 calculations of the H-bond energy, $E(\text{cis/trans})$, and of the change in



(a)



(b)

Figure 2. The same scatter plot as in Figure 1 but only for (a) longer H-bonds, with O...H distance $> 1.3 \text{ \AA}$, and (b) shorter H-bonds, with O...H distance $< 1.3 \text{ \AA}$

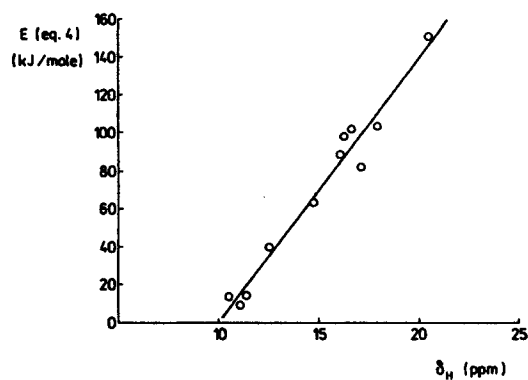


Figure 3. Relationship between energies of O...H interaction estimated using equation (4) and IR $\nu(\text{OH})$ band location

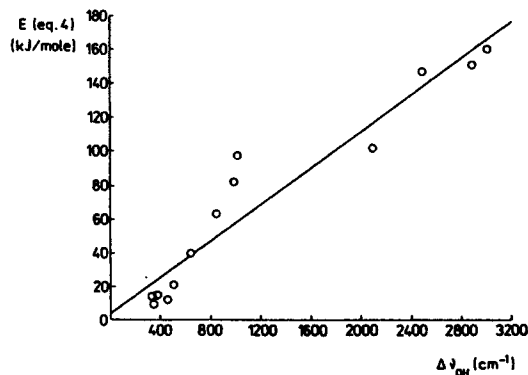


Figure 4. Relationship between energies of O...H interactions estimated using equation (4) and proton NMR chemical shifts, δ_{H}

Table 1. Energies of intramolecular H-bonds in *ortho*-substituted phenol derivatives, E [equation (4)], $E_{\text{cis/trans}}$ change in proton charge density, Δq , and O...H distances

Compound	$R_{\text{H}\cdots\text{O}}$ (\AA)	E [equation (4)] (kJ mol^{-1})	$E_{\text{cis/trans}}$ (kJ mol^{-1})	Δq
<i>o</i> -Hydroxyquinone	2.448	0.728	11.304	0.0024
<i>o</i> -Methoxyphenol	2.086	3.500	6.984	0.0136
<i>o</i> -Hydroxyphenol	2.085	3.515	6.86	0.0144
Methyl salicylate (<i>anti</i>)	1.605	28.201	32.541	0.0369
Salicylamide	1.432	59.730	64.197	0.1079
Salicylic acid	1.404	67.474	64.444	0.1116
Salicylaldehyde	1.396	69.978	46.594	0.1051
<i>o</i> -Hydroxyacetophenone	1.385	73.239	55.584	0.1149
Methyl salicylate (<i>syn</i>)	1.379	75.170	67.758	0.1185

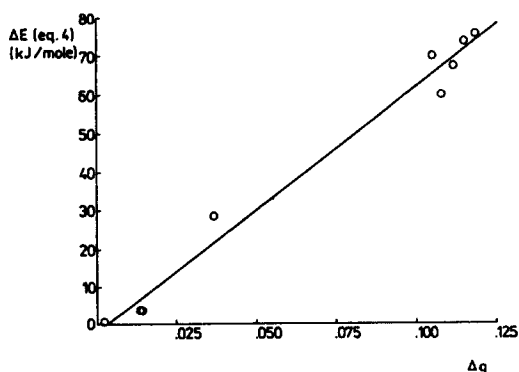


Figure 5. Relationship between energies of O...H interactions estimated using equation (4) and INDO-calculated changes of charge at H-atom

charge at the hydrogen atom in the bridge, $\Delta q(\text{H})$, for a sample of *ortho*-substituted phenols and compared them with the energies calculated using equation (4). The intramolecular H-bond energy, $E(\text{cis/trans})$, was calculated as the difference between the total energy of the conformer with (*s-cis*) and without (*s-trans*) the intramolecular H-bond, assuming the same geometry of the molecule except for the H-bond itself. Table 1 presents all these data together with H...O interatomic distances. Figure 5 shows the plot of $E[\text{equation (4)}]$ vs $\Delta q(\text{H})$, in which Δq may be assumed to be proportional to the H-bond energy,¹⁸ and Figure 6 shows the relationship between $E[\text{equation (4)}]$ and $E(\text{cis/trans})$. The correlation coefficients are 0.991 and 0.955, respectively.

For almost the same sample we compared the two-centre, one-electron energy, $E_{\text{H}\cdots\text{O}}$, calculated by

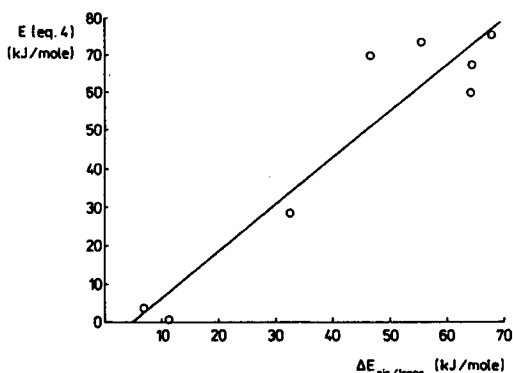


Figure 6. Relationship between energies of O...H interactions estimated using equation (4) and CNDO/2-calculated energy for *cis/trans* change of conformation with H-bond formation in the *cis* state

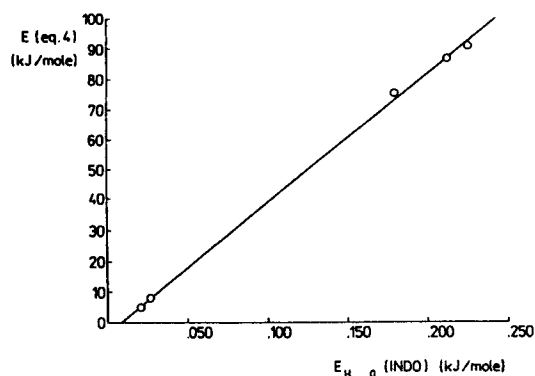


Figure 7. Relationship between energies of O...H interactions estimated using equation (4) and two-centre, one-electron energies, $E_{\text{H}\cdots\text{O}}$, calculated by INDO

INDO⁴ with the data obtained using equation (4). The results obtained are presented in Figure 7; the correlation coefficient for this plot is 0.999.

CONCLUSIONS

Comparison of the energy of H...O interaction estimated directly from the experimental H...O interatomic distance using equation (4) with the results obtained by use of other methods and models leads to the following conclusions: (i) equation (4) can be accepted as giving reliable but approximate information about the energy of H...O interactions; (ii) in families of structurally similar systems there is good qualitative agreement between the results obtained using equation (4) and other data used to describe the H-bond energy; and (iii) owing to ready access to considerable geometrical information from x-ray and neutron diffraction determinations of molecular geometries, a simple extrapolation equation such as equation (4), is very useful, particularly in view of fundamental difficulties in estimating intramolecular H-bond energies.

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