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EFFECT OF HYDROGEN BONDING ON THE THERMAL BEHAVIOUR OF SUBSTITUTED PHENOLS

SALMAN R. SALMAN *

Chemistry Department, College of Science, University of Baghdad (Iraq)

KAFAA F. ABAS

Petrolum Research Centre, Scientific Research Council, Baghdad (Iraq)

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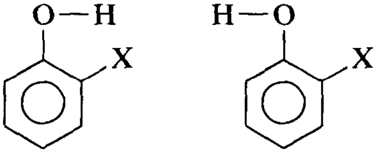
ABSTRACT

The differential thermal analysis of five substituted phenols and two substituted anisols were recorded. The heat of fusion and heat of decomposition, ΔH_m and ΔH_d, were compared with the proton NMR of the hydroxyl chemical shift. It was found that the trend of the hydrogen bond strength in those phenols measured by DTA correlate well with the ^{1}H NMR values of δ_{OH}.

INTRODUCTION

Substituted phenols can exist in two forms, **a** and **b** [1–5].



a **b**

(Formula 1)

When X is a proton acceptor, an intramolecular hydrogen bond (IMHB) will form. The proton NMR chemical shift of the hydroxyl proton, δ_{OH}, is a good measure of the IMHB strength [6–8]. The IMHBS resist the effects of change in temperature and solvent [9]. However, when the population of conformer b increases, δ_{OH} becomes more sensitive to solvent polarity [10]. Substituting a methyl group in position 3 increases the IMHB strength [11,12], but decreases the stability of the hydroxyl towards polar solvents

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* Author to whom correspondence should be addressed.

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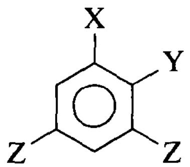
[13]. The values of δ_{OH} in substituted phenols in non-polar and polar solvents could be used as an indication of intra- and intermolecular hydrogen bonding.

On the other hand, the values of the heat of fusion ΔH_m, and heat of decomposition ΔH_d in hydrogen-bonded phenols [7] could be used as a probe for the strength of the hydrogen bonding [3]. No work has been done on the relationship between the thermodynamic values obtained from DTA and the proton chemical shift measured by NMR. The aim of this work is to study the proton NMR and DTA of substituted phenols and anisols (Formula 2) and to use them as a probe for understanding hydrogen bond strength within this series.



(Formula 2)

EXPERIMENTAL

Solutions of compounds **1**–**7** (see Table 1) were prepared in 5 mm NMR tubes at 0.3 mol% in cyclohexane-d_{12} and DMSO – d_6 and their proton NMR were measured on a Varian FT 80 A machine. All compounds, except **2**, are new and their preparation is described elswhere [14]; their structural identification was established by proton NMR, IR spectroscopy and microanalysis. The purity of all samples was checked by GLC.

DTA measurements were carried out on a Heraeus TA-500 thermal analyser under static air. The heating rate was $10\,^\circ C\ min^{-1}$. Naphthalene was used as a reference. The experimental error was $\pm 3\,^\circ C$. The thermodynamic properties of compounds **1**–**7** were calculated according to the method given by David [15].

RESULTS AND DISCUSSION

Table 1 presents the thermodynamic values of compounds **1**–**7**, while Table 2 shows the δ_{OH} values of compounds **1**–**5**. Figures 1 and 2 show the DTA curves of compounds **1**–**7**. From Tables 1 and 2, the following observations and conclusions can be made.

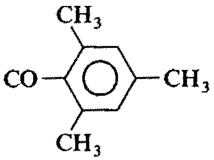
(1) There is a good agreement between the T_m obtained from DTA curves and the m.p. of compounds **1**–**7**.

(2) The δ_{OH} in the cyclohexanes represents the IMHB strength in those

TABLE 1

Thermodynamic properties of compounds **1–7**

Compd. No.	X	Y	Z	T_m [b] (°C)	T_d (°C)	ΔH_m (kJ mol^{-1})	ΔH_d (kJ mol^{-1})	ΔS_m (kJ mol^{-1})	ΔS_d (kJ mol^{-1})
1	OH	$COCH_3$	CH_3	60 (60)	246	1.364	2.929	0.669	1.097
2	OH	COPh	H	35 (37)	253	0.665	1.092	0.428	0.461
3	OH	COPh	CH_3	132 (134)	255	0.674	1.134	0.387	0.502
4	OH	COMes$^+$ [a]	H	80 (82)	284	0.494	0.816	0.564	0.768
5	OH	COMes$^+$ [a]	CH_3	107 (116)	295	0.837	1.088	0.589	1.237
6	OCH_3	$COCH_3$	CH_3	50 (48)	249	0.987	1.029	0.545	0.918
7	OCH_3	COPh	H	77 (77)	315	0.678	1.075	0.466	0.485

[a] COMes$^+$ = CO 

[b] M.p. in parentheses.

TABLE 2

Proton chemical shift of the hydroxyl proton δ_{OH} (ppm) in cyclohexane and DMSO

Compd. No.	δ_{OH} in C_6D_{12}	δ_{OH} in DMSO	$\Delta\delta_{OH}$ [a]
1	12.41	9.79	2.62
2	11.87	10.48	1.39
3	9.54	9.41	0.13
4	11.68	11.94	0.26
5	12.88	10.84	2.04

[a] $\Delta\delta_{OH} = \delta_{OH,cyclohexane} - \delta_{OH,DMSO}$.

compounds. The intramolecular hydrogen bond strength decreases in the following order: **5** > **1** > **2** > **4** > **3**.

(3) The $\Delta\delta_{OH}$ values represent the effect of the solvent on compounds **1**–**5** which represents the intermolecular hydrogen bonding which decreases in the following order; **1** > **5** > **2** > **4** > **3**.

(4) ΔH_m is the heat needed to overcome the intermolecular association. The ΔH_m values for compounds **1**–**5** decrease in the following order: **5** > **1** > **3** > **2** > **4**. With the exception of compound **3**, there is a complete agreement between the DTA and NMR values (see (2) above).

(5) The heat needed for the decomposition of compounds **1**–**5** is used to

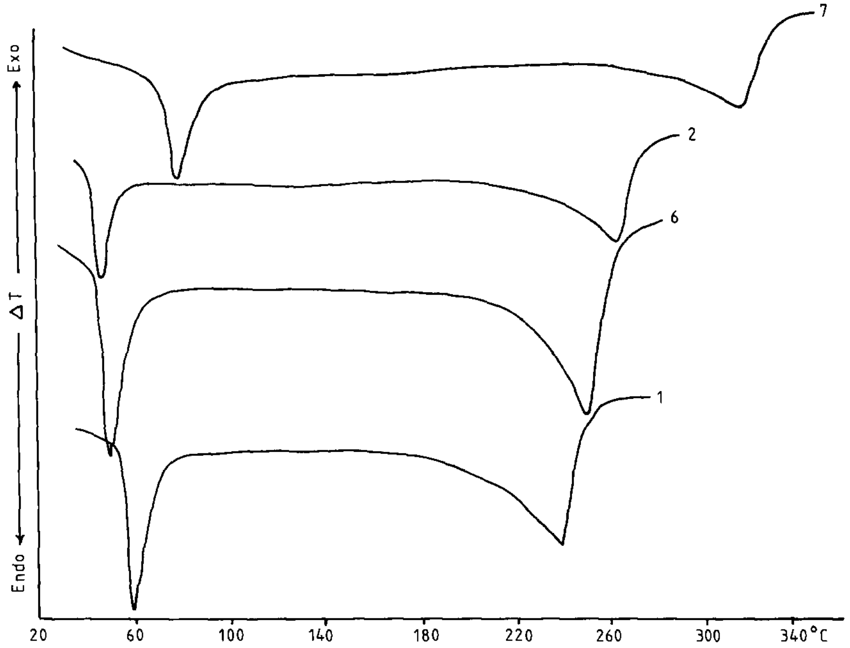


Fig. 1. DTA curves of compounds **1**, **2**, **6** and **7** in static air.

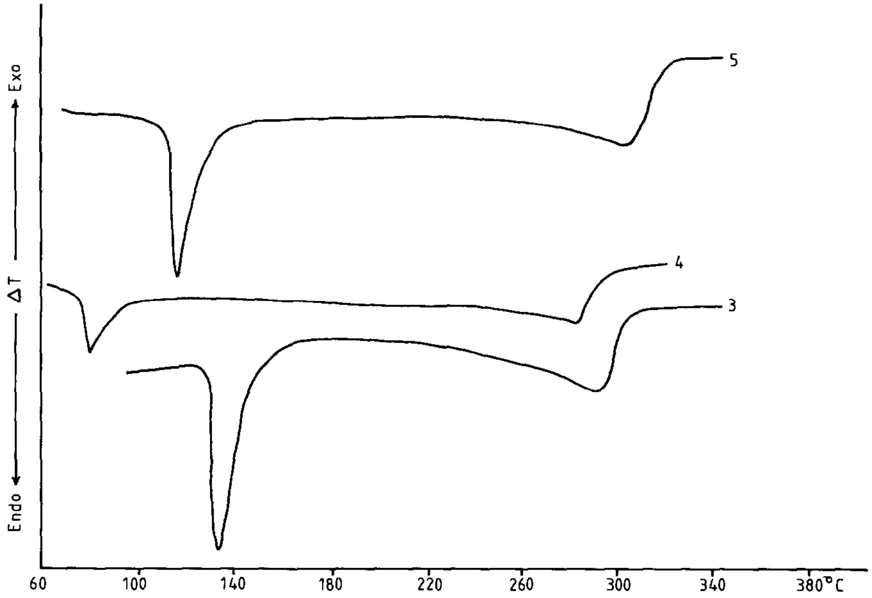


Fig. 2. DTA curves of compounds **3**–**5** in static air.

overcome the inter- and intramolecular hydrogen bonding. The ΔH_d values decrease in the following order: **1** > **3** > **5** ≈ **2** > **4**. If compound **3** is excluded, this result is in good agreement with the NMR result, see (3) above.

(6) The ΔH_d difference between compounds **1** and **6** is large, while it is very small between compounds **3** and **7**. This reflects the fact that the intra- and intermolecular hydrogen bonding in compound 1 is large, while it is very small in compound **3**.

(7) Steric crowding increases the values of ΔH_m and ΔH_d (compare compound **4** with **5** and compound **2** with **3**).

In conclusion, it seems that the values of ΔH_m and ΔH_d obtained from DTA reflect a trend similar to that obtained from ^{1}H NMR concerning the intra- and intermolecular strengths in the substituted compounds investigated.

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