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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, Baghdad (Iraq)

KAFAA F. ABAS

Petroleum Research Center, Scientific Research Council, Baghdad (Iraq)

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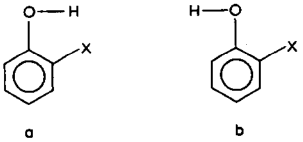
ABSTRACT

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

INTRODUCTION

Substituted phenols can exist in two forms, (a) and (b) [1–5], as shown in Scheme 1. When X represents a proton acceptor an intramolecular hydrogen bond (IMHB) will form. The proton NMR chemical shift δ_{OH} of the hydroxyl proton is a good measure of the IMHB strength [6–8]. The IMHB resists the effect of changes in temperature and solvent [9]. On the other hand, when the population of conformer (b) (Scheme 1) increases δ_{OH} will become more sensitive to solvent polarity [10]. Substituting a methyl group in position 3 increases the IMHB strength [11,12], but decreases the stability



Scheme 1

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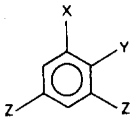
* Author to whom correspondence should be addressed.



Scheme 2

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

Alternatively, values for 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 hydrogen bonding [3]. No work has been done on the relation of thermodynamic values obtained from DTA and proton chemical shifts measured by NMR techniques. The aim of this work is to study the proton NMR and DTA of substituted phenols and anisols (Scheme 2) and to use them as a probe for understanding hydrogen bond strength in this series.

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 elsewhere [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 an Heraeus TA-500 thermal analyser under static air. The heating rate was 10°C min^{-1}. Naphthalene was used as a reference. The experimental error was ±3°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 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 T_m obtained from DTA curves and the m.p. of compounds **1**–**7**.

(2) δ_{OH} in cyclohexane represents the IMHB strength in those compounds. The IMHB strength decreases in the following order: **5** > **1** > **2** > **4** > **3**.

TABLE 1

Thermodynamic properties of compounds **1–7**

Compound	X	Y	Z	T_m (°C) (m.p.)	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[a]	H	35 (37)	253	0.665	1.092	0.428	0.461
3	OH	Coph[a]	CH_3	132 (134)	255	0.674	1.134	0.387	0.502
4	OH	CoMes[b]	H	80 (82)	284	0.494	0.816	0.564	0.768
5	OH	CoMes[b]	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[a]	H	77 (77)	315	0.678	1.075	0.466	0.485

[a] ph = phenyl.

[b] CoMes =

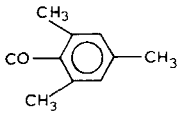


TABLE 2

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

Compound	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 $- \delta_{OH,DMSO}$.

(3) $\Delta\delta_{OH}$ represents the effect of the solvent on compounds **1**–**5** and also 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. ΔH_m values for compounds **1**–**5** decrease in the following order: **5** > **1** > **3** > **2** > **4**.

If we exclude compound **3**, there will be a complete agreement between DTA values and NMR values (see above).

(5) The heat needed for the decomposition of compounds **1**–**5** is used to overcome the intermolecular and intramolecular hydrogen bonding. ΔH_d values decrease in the following order: **1** > **3** > **5** ≈ **2** > **4**.

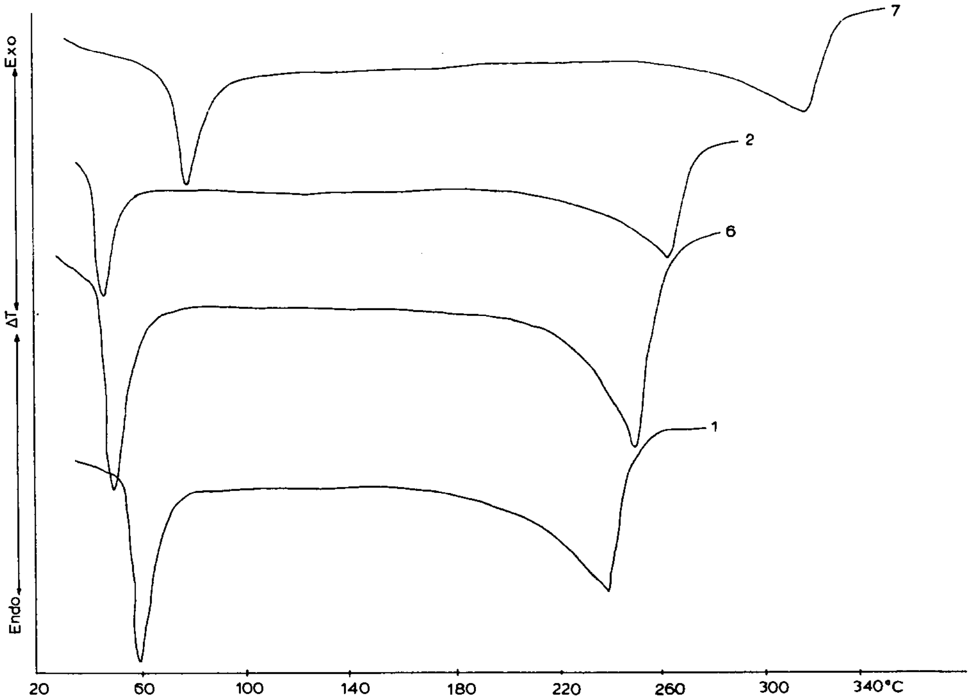


Fig. 1. DTA curve of compounds **1**, **2**, **6** and **7** in static air.

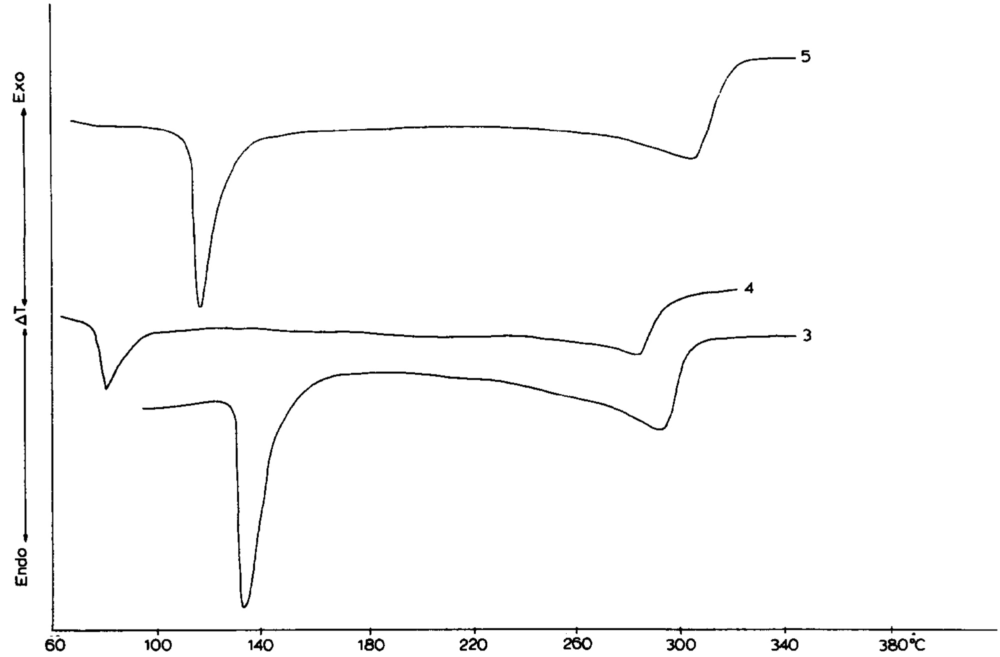


Fig. 2. DTA curve of compounds 3–5 in static air.

If compound **3** is excluded, this result is in good agreement with the NMR (see 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 intramolecular 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 values of ΔH_m and ΔH_d obtained from DTA reflect a trend similar to that obtained from ^{1}H NMR concerning intramolecular and intermolecular strength in the present series.

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