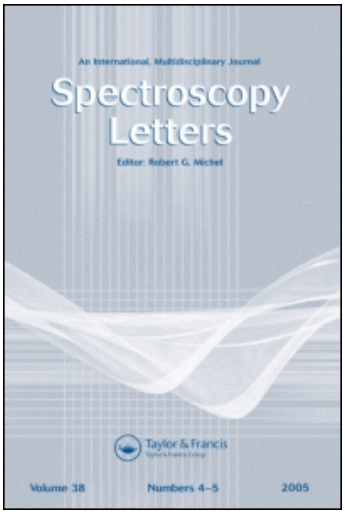

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Similarity Between Some Substituted Phenols Using Pattern Recognition and Multivariate Analysis.

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Similarity Between Some Substituted Phenols Using Pattern Recognition and Multivariate Analysis .

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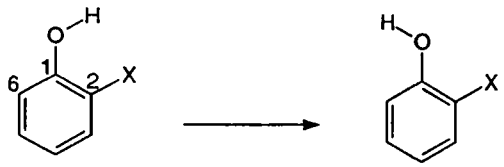
ABSTRACT :

Two series of substituted phenols were prepared and their physical and spectral properties were determined . Multivariate and principle component analysis were use . It was found that statistical method show similarities between different substituted phenols and indicated some correlation between physical and spectral properties .

INTRODUCTION :

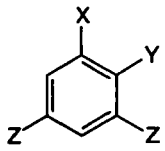
Substituted phenols exists in two forms (a) and (b) (Scheme 1) (1-5) . When we substitute X with a COR group a strong intramolecular hydrogen bonding (IAMHB) will form between the hydroxyl proton and the carbonyl oxygen . The proton chemical shift of the hydroxyl proton , δ_{OH} , can be a good measure for the IAMHB (6-8) . IAMHB will resist the effect of solvent polarity (9) and temperature changes . On the other hand increasing the percentage of (b) conformer make δ_{OH} more sensitive toward solvent polarity (10) . Substitution of a methyl group in position 3 increase the IAMHB strength (11-13) , but in the same time decrease the stability of the IAMHB between hydroxyl proton and the carbonyl oxygen toward polar solvents . In this communication two series of substituted phenols were prepared (Scheme 2) .

In a previous work (14-15) we tried to find a relationship between δ_{OH} and each of the retention time (14) , thermal and thermodynamic properties such as heat of fusion Tm , heat of decomposition Td , enthalpy of fusion ΔHm , enthalpy of decomposition ΔHd , entropy of fusion ΔSm and entropy of decomposition ΔSd (15) . From thermal , NMR and chromatographic data we



[a] [b]

[Scheme 1]



	X	Y	Z
1	OH	$COCH_3$	CH_3
2	OH	COPh	H
3	OH	COPh	CH_3
4	OH	COMes	H
5	OH	COMes	CH_3
6	OCH_3	$COCH_3$	CH_3

[Scheme 2]

obtain a fair order of the strength of IAMHB and intermolecular hydrogen bonding (IMHB) , but it was difficult to classify those compounds according to two variables .

Multivariate statistics enable us to analysis complex set of data and to find similarities between different sets . It is important to use variables and properties specific to each compound in a group of compounds in order to investigate and classify our compounds . Unsupervised methods , such as principle component maps were used to assist in the classification of our samples . The unsupervised approach allows the reduction of n-dimensions parameters descriptors of each compound down to two or three dimensions (16). Hierarchical cluster analysis allow us to find similarities between the compounds according to their properties . The aim of this communication is

Table 1 , List of different variables for compounds 1-6 .

	Compound NO					
Variable	1	2	3	4	5	6
Tm °C	60.0	37.0	134.0	82.0	116.0	48.0
Td °C	246.0	253.0	255.0	284.0	295.0	249.0
ΔHm*	1.364	0.665	0.674	0.494	0.837	0.987
ΔHd*	2.929	1.092	1.134	0.816	1.088	1.029
ΔSm*	0.669	0.428	0.381	0.564	0.589	0.545
ΔSd*	1.097	0.461	0.502	0.768	1.237	0.918
δ_{OH}(B)+	12.41	11.87	9.54	11.68	12.88	0.00
δ_{OH}(D)+	9.79	10.48	9.41	11.94	10.84	0.00
$\Delta\delta_{OH}$**	2.62	1.39	0.13	0.26	2.04	0.00
OV-101	0.93	2.09	3.03	2.95	4.72	0.00
OV-275	4.00	5.02	12.00	2.20	3.42	0.00
δ_{CH3}(3)**	2.21	0.00	1.85	0.00	1.66	2.21
δ_{CH3}(5)**	2.37	0.00	2.21	0.00	2.22	2.34
δ_{CO}**	204.9	199.9	200.7	203.6	205.6	203.7

*Kj/Mole , ** ppm , +(B) = Benzene , (D) = DMSO

to use the physical , thermodynamic and spectral properties of compounds 1-6 as descriptors and to use multivariate analysis to find if there is similarities between those compounds and if it is possible to classify them into classes . Also our aim is to use those data to enable us to find similarities between the variables classification according to the descriptors properties .

EXPERIMENTAL :

The preparation of compounds 1-6 are done according to literature (17) and are given elsewhere (14,17) . The proton coupled and decoupled ^{13}C spectra were recorded on a varian FT 80 MHz spectrometer in CDCl3 with TMS as an internal reference . The ^{1}H NMR was recorded on the same machine and in two solvents , benzene-d6 and DMSO-d6 . Differential thermal analysis (DTA) measurements were carried out on a Heraeus TA-500 thermal analyzer under static air (15) , while a Pye Model 104 gas

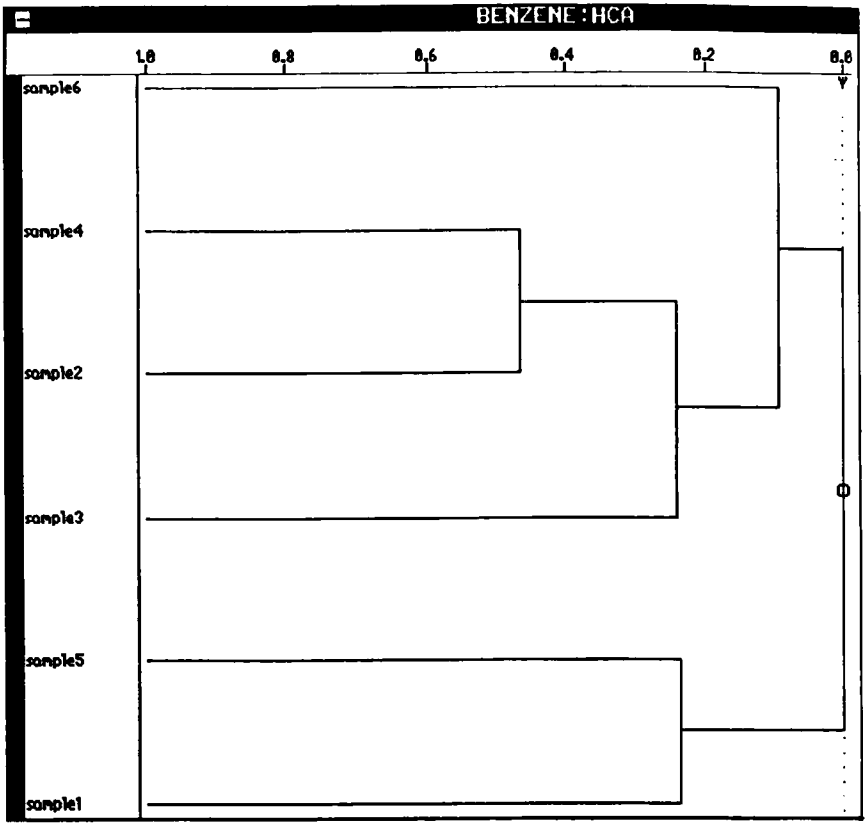


Fig 1 ,Dendogram for samples 1-6 .

Chromatography with dual flame ionization detector (Pye Unicam , Cambridge UK) was used (14) . Two column are used . A non polar OV-101 and a polar OV-275 . Multivariate analysis was carried out using the PC based software Einsight (18) . All properties were auto scaled to a mean of zero and a variance of unity where appropriate before multivariate analysis is performed (16) .

RESULTS and DISCUSSION :

Table 1 show the physical , thermodynamic and spectral data for compounds 1-6 which was used as descriptors . Those variables are melting

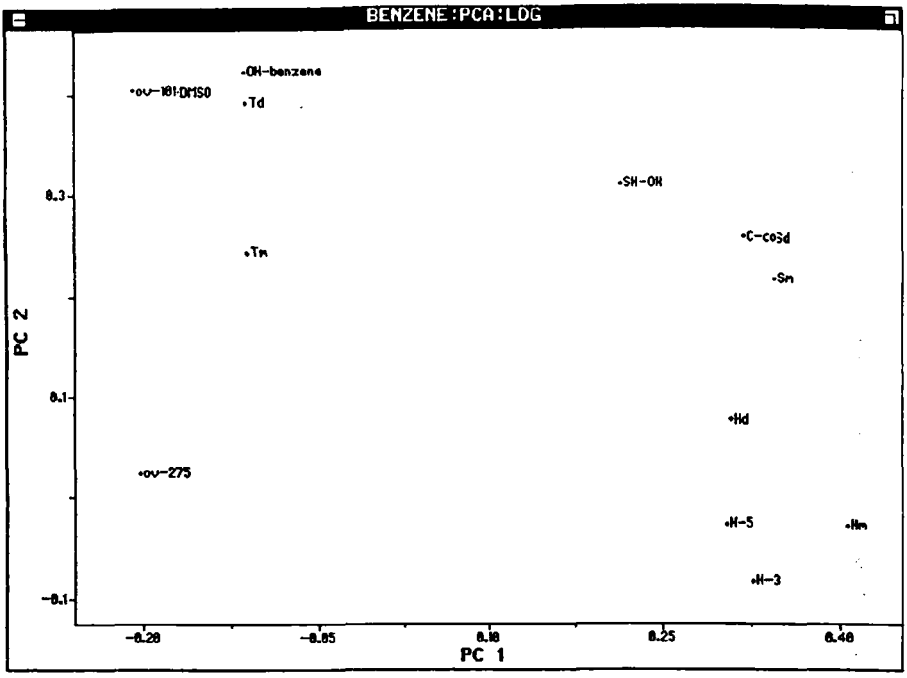


Fig 2 , Relationship between principle component 1 & 2 for the variables .

point (Tm) , decomposition temperature (Td) , enthalpy of fusion ΔHm , enthalpy of decomposition ΔHd , entropy of fusion ΔSm , and of decomposition ΔSd , proton chemical shift δ_{OH} for the hydroxyl proton in benzene and in DMSO , and the difference between δ_{OH} in phenol and in compound 1-6 , $\Delta\delta_{OH}$, the proton chemical shift for the methyl protons δ_{CH3} at positions 3 and 5 (H-3 and H-5) , the ^{13}C chemical shift of the carbonyl group δ_{CO} in compounds 1-6 , and the retention time using polar and non polar columns . All those parameters are used as descriptors on the bases that in compounds 1-6 there are the following : IAMHB between the hydroxyl proton and the carbonyl group . This IAMHB manifest itself in a low field shift for the hydroxyl proton and the carbonyl group relative to their values in unsubstituted compounds .

Intermolecular hydrogen bonding (IMHB) between the hydroxyl proton and the solvent , this manifest itself in a high field shift of the hydroxyl proton relative to its position in the mother molecule 1-5 .

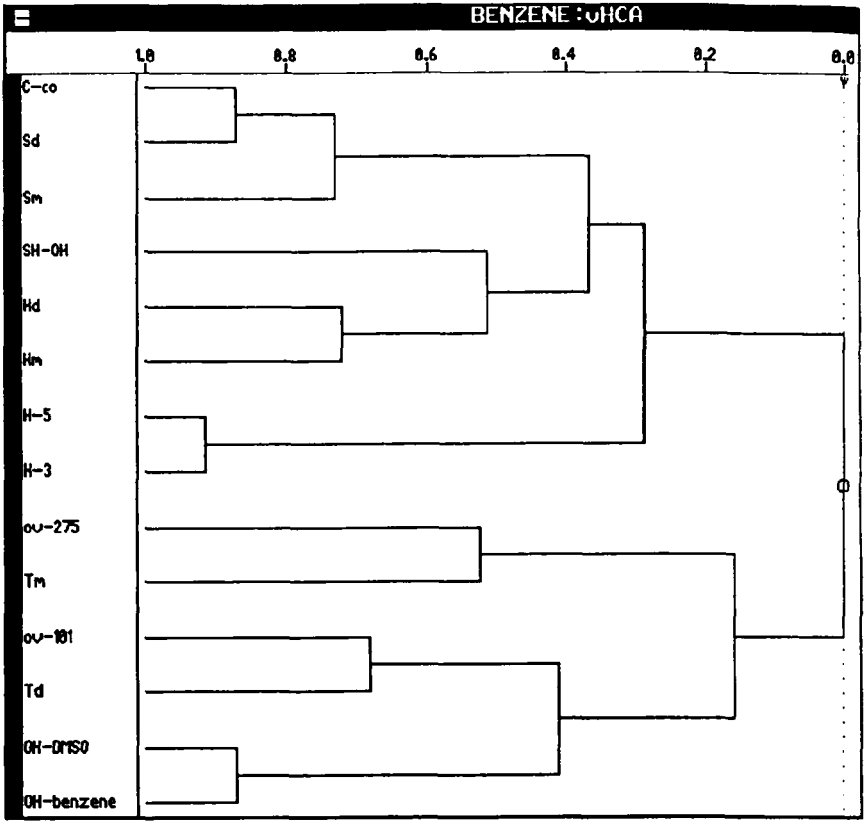


Fig 3 , Dendogram for the variables .

Steric effect of the methyl group at position 3 will cause conformational changes for the substituents at position 2 . This conformational changes for each molecule will manifest itself in changes in the physical , thermodynamic and spectral parameters .

The unsupervised approach using dimensional reduction and mapping method show the following features . The first three principle components (PC) accounts for 82 % of the variance in the data with the first two PC contributing 65 % to the variance . Fig 1 show the result of the hierarchical cluster analysis for compounds 1-6 . It is interesting to see that samples 2 , 3 and 4 cluster together with a higher similarity between compounds 2 and 4.

Samples 1 and 5 cluster together while compounds 6 show no similarity to any compound in the two series . This may indicates that the IAMHB between δ_{OH} and δ_{CO} in compounds 2 and 4 is responsible for the behavior of those compounds toward other parameters like thermal and chromatographic effect . Geometrical and conformational changes do contribute to a variable degree in decreasing the similarity to about 0.5 . As for compounds 1 and 5 both of them are affected by steric and conformational factors and those factors decrease the similarity between those two compounds to about 0.3 , thus indicating the importance of steric effect in determining the physical and spectral properties of such compounds . It is also interesting to note that compound 3 cluster with compound 2 and 4 and not with compounds 1 and 5 indicating that steric effect is not as large as it is in compound 5 . Figure 2 show the relation between PC1 and PC2 for the variables . From this diagram it seem that two cluster was obtained , the first includes the chemical shift of the methyl group at positions 3 and 5 , ΔHd , ΔHm , ΔSm and δ_{CO} , the second cluster includes Tm , Td , δ_{OH} (DMSO) , δ_{OH} (benzene) , OV101 and OV275 cluster together . Fig 3 show the dendogram of the variables and it is interesting to note the large similarity between δ_{CH3} at position 3 and δ_{CH3} at position 5 , between δ_{OH} (DMSO) and δ_{OH} (benzene) , between δ_{CO} , ΔSd and ΔSm . Similarity between the two variables δ_{OH} and ΔSd is very interesting because the carbonyl chemical shift is highly affected by conformational and geometric changes (12,13) and ΔSd is an indicator of the changes in order during fusion and decomposition .

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