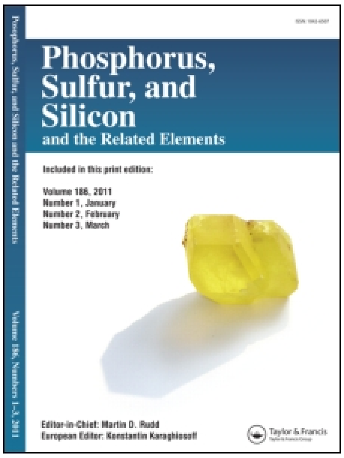

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Jøgart, Tommy , Andresen, Birgit and Duus, Fritz(1991) 'SOLVENT AND SUBSTITUENT INFLUENCE ON THE CHELATE PROTON NMR CHEMICAL SHIFT OF AROMATIC β-THIOXOKETONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 59: 1, 181 — 184

To link to this Article: DOI: 10.1080/10426509108045719

URL: http://dx.doi.org/10.1080/10426509108045719

Phosphorus, Sulfur, and Silicon, 1991, Vol. 59, pp. 181-184
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SOLVENT AND SUBSTITUENT INFLUENCE ON THE CHELATE PROTON NMR CHEMICAL SHIFT OF AROMATIC β-THIOXOKETONES.

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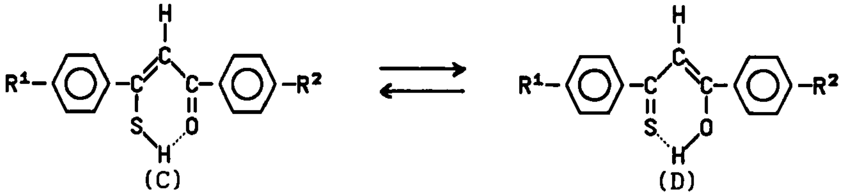
Abstract The enol-enethiol tautomerism of p/p'-disubstituted thiobenzoyl benzoyl methanes have been studied by ^1H NMR spectroscopy. The significance of the chelate proton chemical shift has been evaluated by means of principal component analysis.

INTRODUCTION

β-thioxoketones are of interest as model compounds for studies of intramolecular hydrogen chelation. Some investigations, especially on non-aromatic β-thioxoketones, have been done.[1] In solution, these compounds have been found to exist entirely as a mixture of the (Z)-enol form and the (Z)-enethiol form.[1] The interconversion between these two forms, which is very rapid (on the NMR time scale), takes place by intramolecular chelate proton transfer, and gives rise to the observation of a weighted average NMR spectrum.

This work describes an attempt to clarify the structural dynamics of β-thioxoketones having aromatic flanking groups:


(C)
(D)

We have chosen to focus on the chelate proton chemical shift because of its significance as a reflector of the site of the enol-enethiol equilibrium.[1] Particularly, we have tried to variation in substituent R^2 (fig.2), and 8 21-dimensional vectors representing the solvent variation.

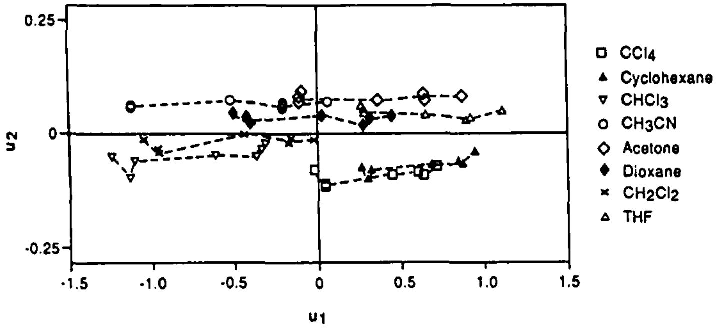


FIGURE 1 56 vectors representing variation in R^2 substituent and solvents.

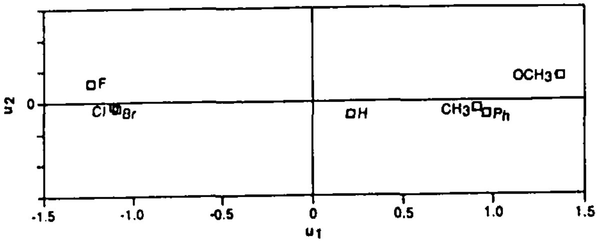


FIGURE 2 7 vectors representing variation in R^2 substituent.

DISCUSSION

Fig.1 shows the subspace spanned by the two most prominent eigenvectors u_1 and u_2. This subspace represents 99.96 percent of the variation. The first eigenvector alone represents 99.02 percent of the variation. Fig.1 visualizes how the R^2 substituents and the solvents give separable effects: 8 solvent series of 7 vectors representing different R^2 substituents are distinguished. Because of the prominent variation along u_1, we conclude that the R^2 substituents and the solvents fundamentally affect the chelate proton chemical shift by the same mode.

The importance of the substituent R^2 is shown in fig.2, where u_1 takes up 99.36 percent of the variation, and u_2 takes up 0.52 percent of the variation. Because the variation is so convincingly represented by one single vector, it can be concluded that any determine quantitatively, how this shift is influenced by intramolecular factors (the nature of the R^1 and R^2 substituents) and by extramolecular factors (the solvent).

Assuming that the chelate proton chemical shift primarily depends on the location of the C ⇄ D equilibrium, we can write the following equation:

$$\delta(R^1, R^2, \text{solvent}) = x_C\delta_{SH} + (1-x_C)\delta_{OH} \qquad (1)$$

where $\delta(R^1,R^2,\text{solvent})$ is the observed chelate proton chemical shift (at infinite dilution), x_C is the mole fraction of the tautomer C at tautomeric equilibrium, δ_{SH} is the hypothetical chelate proton shift of C at infinite solution, and δ_{OH} is the hypothetical chelate proton shift of D at infinite solution.

For simple non-aromatic β-thioxoketones, it has been found that flanking groups function as equilibrium regulators. Also, the solvent has been found to influence the equilibrium, and a clear dependency of δ_{OH} and δ_{SH} on the solvent has been recognized.[1]

A series of 21 p/p′-disubstituted thiobenzoyl benzoyl methanes have been synthesized and studied by ^{1}H NMR spectroscopy in 8 different solvents. The R^1 substituents are H, Me and OMe; the R^2 substituents are H, Me, Ph, OMe, F, Cl, and Br. The solvents are tetrachloromethane, cyclohexane, chloroform, acetonitrile, acetone, 1,4-dioxane, dichloromethane, and tetrahydrofuran.

Because of the large number of data (168 chelate proton chemical shifts), principal component analysis (PCA) have been used.[2] The data have been organized in several ways. For example, 56 3-dimensional vectors collectively representing all possible variation in R^2 as well as all applied solvents, were made by using as coordinates the three δ-values reflecting the variation in R^1. In this way, the R^1-variation is included in every vector, and cannot, accordingly in itself be represented in the graph (fig. 1). Several other ways to organize data were also experienced. Two of these are of particularly informative value, namely the collection of 7 24-dimensional vectors representing the substituent R^2 affects the chelate proton chemical shift in almost the same way, independently of the precise nature of R^1 and the solvent. The difference is only a matter of degree. Furthermore, fig.2 displays a very characteristic order of the substituents R^2: $F < Cl \leq Br < H < Me < Ph < OMe$.

We have found a relationship between the coordinate values of the 7 substituents along u_1 and the Hammett substituent parameters σ_I and σ_R+. This indicates transmission of substitution through the aromatic system effecting change in the (Z)-enol (Z)-enethiol equilibrium.

The influence of the solvent was the subject of another PCA. In this subspace, 97.61 percent of the variation is taken up by u_1 and 2.24 percent by u_2. In fig.3, this result has been compared with a PCA of Kamlet-Taft's triplet of solvatochromic parameters (π^*, α, β) and a correspondence is demonstrated.

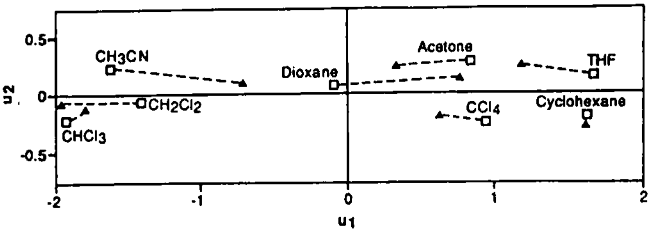


FIGURE 3 Vectors representing solvents in eigenvector subspace (squares). From (π^*, α, β) related values have been computed (crosses).

CONCLUSION

On the basis of this work, we conclude that R^2 as well as the solvent act fundamentally in the same way, i.e. as equilibrium regulators. Moreover, with the existence of 8 different solvent vectors, we conclude that solvents also affect the chelate proton chemical shift by directly affecting δ_{OH} and δ_{SH}.

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