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Electronegativity And Resonance Effects On Identification Of Halogens By NMR, With Using DBM Derivatives And As Well A New La(III) Shift Reagent

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ABSTRACT

A series of complexes of di-tert-butyl 1,3-acetone dicarboxylate and halogenated derivatives dibenzoylmethane (DBM) at ortho, meta and para positions of mono as well as biphenyl rings with praseodymium and europium have been synthesized as lanthanide shift reagents and the induced shifts (LIS) in ¹H NMR spectra on n-pentanol have been studied. More interest is NMR studies of the electro negativity effects and as well the resonance effects of halogens. The order of electro negativity and steric effects of halogens and as well resonance and inductive effects of these substituents in phenyl rings of LSRs have been studied by the observed order of LIS which arises from these shift reagents. It has been observed that the induced shift of protons of n-pentanol increases along increasing of electro negativity effect of substituted halogens i.e. by inductive effects but the resonance effect decreases the induced shifts. And also the result of experiment, comparison the induced shifts of the meta substitution of halogens has shown electronegativity in order of F>Cl>Br>I, as well for the same situation substitution in both rings of DBM in chelate has shown more effect than the substitution in one ring in LIS. As well the resonance effects of halogens has been tested by this manner. A new LSR with using the di-tert-butyl 1,3-acetone dicarboxylate as a ligand has been synthesized and studied as a shift reagents. The lanthanide type and as well solvent effect in LIS also studied. Most lanthanide DBM complexes have been examined as possible shift reagent. A test on the effect of solvents has been done and it has been observed that LIS of the protons of n-pentanol decreases among the series CCl₄>CDCl₃>C₆D₆>(CD₃)₂CO.

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KEYWORDS

Shift reagent;
Dibenzoylmethane
derivatives;
Di-tert-butyl 1,3-acetone
dicarboxylate of La(III).

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INTRODUCTION

Paramagnetic lanthanide β -diketoenolat complexes have been found useful in high resolution NMR studies of organic compounds without using a high frequency spectrometer^[1-3]. Lanthanide shift reagents (LSR's) owe their popularity to the fact that they alter high resolution nuclear magnetic resonance (NMR) spectra in an interpretable fashion. These studies have provided valuable information in areas ranging from solution configuration determination^[4] to the selection of the shift reagent for a given application^[5]. But a large portion of the NMR shift reagent literature devotes relatively little attention to the nature of shift reagent, since the goal of these studies have been synthesized some new LSR as well some new application of such chelates to confirm the order of electro negativity or inductive and as well resonance effect of halogens in phenyl rings of LSRs by NMR method or have been attained the nature of ligand using in LSRs.

The majority of reports on LSR concern the β -diketones^[6-9]. While β -diketones containing halogens in one and two phenyl rings of DBM have attracted considerable attention, and the effect of halogen substituted β -diketones in the form of dibenzoyl methane, as a chelate, has not been much considered yet. In this note, we report the effect of substituted DBM complexes of praseodymium on chemical shifts in ¹H NMR spectra of n-pentanol. Pentanol with six sets of protons has been chosen for investigating the ability of these complexes in proton NMR shift reagents.

In continuation of these studies we decided to study of electro negativity and resonance and as well steric effect of halogens on substituted dibenzoyl methane by NMR method.

The ability of the dibenzoylmethanato Pr and Eu in spreading out and simplifying complicated NMR spectra has been shown^[10]. Our efforts in this field involved a survey the shifting abilities of the series of Pr (4,4'-X DBM)₃ [X = Cl, Br, F] and as well ortho and meta positions of DBM chelates on n-pentanol. Also, we compared the effect of Pr complexes of halogenated on one and two rings of DBM at three positions ortho, meta and para.

EXPERIMENTAL

The praseodymium as nitrate salts, the solvents and other chemicals were obtained from Merck and used without further purification. The ¹H NMR spectra were run on a 60 MHz Varian spectrometer in CDCl₃ and CCl₄. Proton resonance shifts were measured relative to an internal TMS reference. The LIS data are obtained by the incremental addition method, in which the first sample is prepared at the lowest LSR concentration to be run, and subsequent samples are prepared by concentrating with LSR. Melting points were taken on a Stuart melting point apparatus and are uncorrected.

The halogen substitution of dibenzoylmethane (such as p-chlorodibenzoylmethane) was synthesized by a Claisen condensation^[11] of methyl p-chloro benzoate with 4'-chloro acetophenone. At first, 4'-chloro benzoate (0.02M) was mixed with sodium amide (0.04M), diethyl ether (10 ml) and stirred for 15 minutes.

Methyl-p-chlorobenzoate (0.02M) was dissolved in diethyl ether (10 ml) and added to the above solution and refluxed for 2 h. The product was neutralized by 3 M HCl and oily phase extracted by ether and dried using sodium sulphate. To obtain the other derivatives of dibenzoylmethane, the same procedure was adopted except that ester and acetophenone proportional to the product have been chosen. The complexes of lanthanide were isolated by the procedure reported by Biltz et al^[12].

RESULTS AND DISCUSSION

Most of lanthanides have been examined as possible shift reagents. In general europium and praseodymium have proved most suitable for ¹H NMR studies^[13,15]. They minimize the broadening effect, and are complementary since they shift signals in opposite directions. Broadening at low lanthanide concentration is undesirable since it prevents the resolution of small couplings which may be otherwise useful for assignments. The lanthanide type effect in LIS also studied. It has been found that the Eu, Yb, Er complexes show low field shift and Pr, Sm, Nd, Tb, Ce high field shift and Lu, La did not

TABLE 1: Some characteristics of the synthesised lanthanide shift reagents

Name of complex	Chelate	Melting point (°C)	Color	Direction of shift
Tris(dibenzoylmethanato) praseodymium(III)	Pr(DBM) ₃	194 -196	Greenish yellow	high
Tris(4-cholorodibenzoylmethanato) praseodymium(III)	Pr(4-Cl DBM) ₃	212-215	Lemonade	high
Tris(3-cholorodibenzoylmethanato) praseodymium(III)	Pr(3-Cl DBM) ₃	194-196.5	Lemonade	high
Tris(2-cholorodibenzoylmethanato) Praseomidiom(III)	Pr(2-Cl DBM) ₃	155.4	Light cream	high
Tris(2-bromodibenzoylmethanato) praseodymium(III)	Pr(2-Br DBM) ₃	157-158	Dark cream	high
Tris(4-fluorodibenzoylmethanato) praseodymium(III)	Pr(4-F DBM) ₃	230	Yellow	high
Tris(2-choloro,4'-fluorodibenzoyl methanato) praseodymium(III)	Pr(2-Cl ,4'-FDBM) ₃	160-163	Cream	high
Tris(3-choloro,4'-fluorodibenzoyl methanato) praseodymium(III)	Pr(3-Cl ,4'-FDBM) ₃	215-217	Cream	high
Tris(4-choloro,4'-fluorodibenzoyl methanato) praseodymium(III)	Pr(4-Cl ,4'-FDBM) ₃	259-260	Milky	high
Tris(2-bromo,4'-fluorodibenzoyl methanato) praseodymium(III)	Pr(2-Br ,4'-FDBM) ₃	179	Dark cream	high
Tris(2,2'-dicholorodibenzoylmethanato) Praseodymium(III)	Pr(2,2'-Cl DBM) ₃	168	Light green	high
Tris(3,3'-dicholorodibenzoylmethanato)Praseodymium(III)	Pr(3,3'-Cl DBM) ₃	100-102	Yellow	high
Tris(4,4'-dicholorodibenzoylmethanato)Praseodymium(III)	Pr(4,4'-Cl DBM) ₃	95-97	Orange	high
Tris(4,4'-dibromodibenzoylmethanato)Praseodymium(III)	Pr(4,4'-BrDBM) ₃	112	Yellow	high
Tris(4,4'-difluorodibenzoylmethanato)Praseodymium(III)	Pr(4,4'-F DBM) ₃	72	Yellow	high
Tris(dibenzoylmethanato) europium(III)	Eu(DBM) ₃	197.2	Yellow	low
Tris(di-tert butyl acetonedicarboxylat) praseodymium(III)	—	99	Light green	high
Tris(di-tert butylacetone dicarboxylat) europium(III)	—	95	Cream	low
Tris(di-tert butyl acetone dicarboxylat) eterbium(III)	—	162.5	Milky	low
Tris(di-tert butyl acetone dicarboxylat) terbium (III)	—	156	Yellow	high

show any shift. All the lanthanide DBM complexes except Eu, Pr, Yb have shown broaden peaks. In some cases Yb³⁺ complexes may be required to achieve greater spreading of the resonance but these will cause a simultaneous increased in the degree of signal broadening. In studies the solvent type effect in the LIS of proton we observed that the LIS of n-pentanol protons decrease along the following series CCl₄>CDCl₃>C₆D₆>(CD₃)₂CO.

At higher concentrations of lanthanide, broadening becomes a more serious problem, leads to eventual loss of signals; so we studied effects of chelates in two molar ratios, [LSR]/[S], 0.5 and 1. In continuation of our studies on the lanthanide shift reagents (LSR), we have been constantly trying to find some suitable complexes to overcome the resolution problems in NMR without using a high frequency spectrometer.

The LSRs are the coordination compounds which are formed a metal atom as lewis acid and a β-diketone like as DBM acting as a lewis base. The lewis acid is often called the central metal because it is surrounded by the lewis bases. The lewis base is called the ligand. A ligand is simply a species covalently bonded to the central metal atom. When a ligand is polydentate the resulting complex is called a chelate. The vacant sites on lanthanides could accommodate electrons of the substrate. The magnitude of the induced shift depends not only on molar ratio of LSR chelates to substrate, but also on the complex forming strength of the substrate with LSRs, i.e. their ability to act as a lewis base and acid respectively. Embracing the view point that acid-base reactions involve the donation and acceptance of a share in a pair of electrons. A lewis acid, such as lanthanide DBM complexes and their derivatives are

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shown different ability of lewis acid properties (an electron pair acceptor). Lewis bases are electron-pair donor which termed as substrates. Therefore, reactions can take place between the complexes and molecules containing O, N, S atoms with free electron pairs. ($\text{LSR} + \text{S} \leftrightarrow \text{Compound}$), which containing a coordinate covalent bond. The formation of a coordination compound (some times called an adduct) is a lewis acid-base neutralization reaction. The degrees of naturalization lanthanide could be affected the magnitude of the chemical shifts of the nucleus of such substrates. In other words removing electron density from the hydrogen atoms and deshielding the protons, the observed order of shifts arises from the shielding and deshielding effects of the protons in substrate. If we compare the LIS of different halogenated DBM LSRs for the same substrate and as well the same condition, then it will help us to conclude the effect of halogens on phenyl rings of $(\text{DBM})_3\text{La}$ and/or consider the order of inductive and resonance effect of halogens by NMR method.

The results in TABLE 2 (see the rows of 1-4), shows that by using various substituents of DBM, the observed shifts in n-pentanol are increased by a significant factor at meta position of halogens, as compared to ortho and para positions. And also the analysis of the observed shifts in terms of the efficiencies of halogen substituted in both phenyl rings in three different positions in separating of the proton resonance shows that the observed selective shifts in n-pentanol are increased by a significant factor at meta position of halogens, as compared to ortho and para positions (rows of 1,7,8,9 in TABLE 2).

This may be attributed to the steric as well as Lewis-basic effects of the ligands of LSRs. Smaller shifts for chelates with halogen substituted in both rings in ortho and para positions are due to their poorer Lewis-acidity relative to meta position of halogen, which it is attributed to the resonance and positive inductive effects of substituted halogens on the dibenzoylmethane rings. Halogens in meta position on phenyl rings of (DBM) LSR chelates is shown both inductive and resonance effects which can be deduced inductive is more effect than the resonance effect at meta position. And the comparison of the

shifts obtained from ortho and para positions shows greater induced shifts for ortho position and conversely, resonance effects of halogens is more efficient at para position of phenyl rings. In addition, the results obtained show that the transformations of shifts are greater for halogen substituted in both rings; since the significant factor can affected effectively.

In studies the electro negativity effect of halogens (the rows 9-11 of TABLE 2), we found that the induced shifts are larger for fluoro on both phenyl rings chelates with respect to the Cl and Br, and also bromo substituted on both rings chelates induced lower shifts than chloro substituted. Since the order of halogen resonance effect is $\text{F} < \text{Cl} < \text{Br}$ at para position in phenyl rings of lanthanide DBM shift reagents i.e. it was shown that the substitution of halogens on both phenyl rings of DBM decreases the LIS at the above order. In consideration of inductive effects of halogens on meta positions from the LIS conversely to the resonance on para or ortho positions we found the order of $\text{F} > \text{Cl} > \text{Br}$.

We have demonstrated the ability of the halogenated chelates, special fluoro substituted in one and both rings of DBM on meta cause greater shifts than the unsubstituted chelates based on electro negativity effect of halogens. It is attributed to increasing of Lewis-acidity, since chelate can be coordinated to substrate strongly. (see the rows 2 and 6)

In addition of the resonance effect in ortho position, the shifts were obtained for the substituted chelate in ortho position in one or two rings might be restrict with steric prevention as we wish to observe lower shifts in the presence of the bromo substituted instead of chloro or fluoro substituted chelate.

As pointed out in the text books, obviously it has been known that the electron clouds of the π -bonds are highly mobile; for this reason it is only in non substituted benzene C_6H_6 that all the atoms have the same electron density. The entry of substituents e.g. Cl, Br, F, OH or NO_2 causes a considerable redistribution of the electron density in accordance with the nature of the substituents. When the F, Cl, Br, I, atom, linked to the benzene ring, is as rule more distinctly electronegative. The free (unshared)

TABLE 2: Induced shifts of the different protons of pentanol (in ppm) in CCl_4

LIS in ratio of $[\text{LSR}]/[\text{S}]=0.5$					LIS in ratio of $[\text{LSR}]/[\text{S}]=1$					LSR	No.
H ₁	H ₂	H ₃	H ₄	H ₅	H ₁	H ₂	H ₃	H ₄	H ₅		
7.89	4.93	3.13	1.77	1.07	13.32	8.23	5.06	2.75	1.59	Pr(DBM) ₃	1
3.98	2.47	1.81	1.04	0.61	7.45	4.78	3.24	1.88	0.98	Pr(4-ClDBM) ₃	2
9.01	5.36	3.49	1.78	1.08	13.92	8.32	5.25	2.85	1.63	Pr(3-ClDBM) ₃	3
5.00	2.93	2.22	1.24	0.74	7.95	5.13	3.83	1.90	1.46	Pr(2-ClDBM) ₃	4
4.59	2.71	1.92	0.74	0.55	6.6	5.00	3.45	1.25	1.28	Pr(2-BrDBM) ₃	5
7.61	4.56	2.95	1.64	1.93	12.51	7.65	4.69	2.52	1.59	Pr(4-FDBM) ₃	6
4.69	2.61	1.99	1.22	0.68	7.81	4.32	3.46	1.86	1.13	Pr(2,2'-ClDBM) ₃	7
9.16	5.75	3.55	2.33	1.26	14.48	9.88	5.44	3.11	1.65	Pr(3,3'-ClDBM) ₃	8
3.91	1.99	1.28	1.02	0.56	6.66	3.31	1.93	1.68	0.73	Pr(4,4'-ClDBM) ₃	9
6.53	2.02	1.62	1.54	1.07	10.71	3.35	2.50	2.30	1.00	Pr(4,4'-FDBM) ₃	10
2.93	1.03	0.99	0.98	0.54	6.42	2.73	1.78	1.41	0.58	Pr(4,4'-BrDBM) ₃	11

TABLE 3: Induced shifts of the different protons of pentanol (in ppm) in CDCl_3

LIS in ratio of $[\text{LSR}]/[\text{S}]=0.5$					LIS in ratio of $[\text{LSR}]/[\text{S}]=1$					LSR	NO.
H ₁	H ₂	H ₃	H ₄	H ₅	H ₁	H ₂	H ₃	H ₄	H ₅		
-3.26	-1.73	-1.71	-1.58	-0.94	-4.92	-2.47	-2.47	-2.14	-1.28	Pr(C ₁₃ H ₂₂ O ₅) ₃	1
-7.93	-5.02	-4.03	-2.94	-2.33	-10.58	-4.90	-4.90	-3.45	-2.33	Tb(C ₁₃ H ₂₂ O ₅) ₃	2
2.86	1.06	0.65	0.62	0.62	5.05	2.84	1.71	1.05	0.80	Yb(C ₁₃ H ₂₂ O ₅) ₃	3

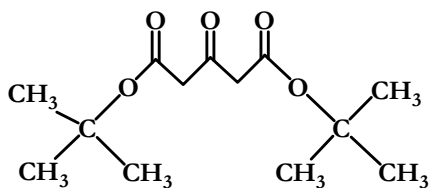


Figure 1: Chemical structure of the di-tert-butyl 1,3-acetone dicarboxylate

electron pairs of the F, Cl, Br, I, atoms increase the electron density of the benzene ring primarily in ortho and para positions (resonance effect) the carbon atoms of the ring which acquire an increase electron density. In substituents of NO_2 or $-\text{COOH}$ or $-\text{SO}_3\text{H}$ linked to the benzene ring, is as a rule more distinctly electropositive than the former. Substituents of the second class, by attracting electron clouds, reduce the electron density in the benzene ring especially in ortho and para positions. This class of derivatives also synthesised and has been tested but we have encountered by a solubility problem, since we can not have a good analysis.

The vacant sites on lanthanides could accommodate the electrons of the substrate. So, on addition of $\text{Ln}(\text{DBM})_3$ to the solution of a substrate, the spectrum becomes amenable to a first order analysis. The substrate associates with the complex at the hydroxyl group. The induced shifts decrease rapidly

by increasing the distance of the protons from the hydroxyl group. In the normal spectrum of *n*-pentanol, the proton resonances of all the methyl groups except that adjacent to the OH group gives rise to a single featureless band in the region δ 2 to 3.6 ppm. On adding $\text{Eu}(\text{DBM})_3$ and $\text{Pr}(\text{DBM})_3$ and as well the new complexes of di-tert-butyl-1,3-acetone dicarboxylato praseodimium have been synthesized and studied as a shift reagents. They have shown the induced shift effects and the first order analysis became possible (see TABLE 2 and 3).

TABLE 3 shows the LIS of the di-tert-butyl-1,3-acetone dicarboxylate (see figure 1) of various LSRs on pentanol and indicates the variation in the magnitude and direction of the induced chemical shifts which related to the chelate and the kind of lanthanides. As the same results as the β -diketone LSRs the di-tert-butyl-1,3-acetone dicarboxylato terbium has shown the greatest induced shift with respect to the other lanthanides.

CONCLUSION

From the obtained results of our studies it should be concluded:

- 1 The ligands type affects the value of LIS.
- 2 The resonance effect of halogens reduces the value of LIS.

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- 3 The positive inductive effect increases the value of LIS.
- 4 The resonance effect of halogens decreases along increasing the electro negativity of halogens and the inductive effect increases along increasing the electro negativity.
- 5 The steric effect of the substituted halogens reduces the value of LIS, specially in ortho position.
- 6 The resonance effect is greater in ortho and para positions, since the para is affected than the ortho position.
- 7 The inductive effect is greater in meta position.

The observed order of shifts arises from the halogen substituted chelates of (DBM) La_3 could be used for demonstrating the order of electro negativity of halogens and as well for the resonance effects of substituents in phenyl ring of DBM.

The studies of the shift behavior of these LSR_s on n-pentanol shows that the meta substitution of halogens has shown more shift effect compared to ortho and para substitution even relative to unsubstituted DBM LSR_s .

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