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A review on NMR spectra during study of interaction ofditertiary butyl chromate with six membered monocarboxylic acid and dicarboxylic acid

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Abstact : In NMR spectra carboxylic proton shows signals at 10.5 to 15 ppm and aldehydic proton shows signals at 9 to 10 ppm but the signals may be shifted downfied or upfield depending upon the environment of proton (shielding and deshielding). In this research paper it has been tried to explain the shift (upfield or downfield) of carboxylic, aldehydic and other protons due to interaction with ditertiary butyl chromate (TBC) by taking the example of six membered monocarboxylic acid (caproic acid) and dicarboxylic acid (adipic acid) in different molar ratio substratre : reagent.

Keywords: TBC (di-tertiary butyl chromate), NMR (nuclear magnetic resonance), CB2, CB4, AB2, AB4 (name of samples).

Introduction:[1-5] The values of chemical shift may lower or higher than the expected values depending upon the environment of proton. These can be explained as follows:

1. Sigma electrons shield the nucleus and the proton absorbs at higher field. Alkyl groups are electron donating. Methyl groups usually absorb at 0.9 ppm, -CH_2- groups (methylene) are found at about 1.1-1.3 ppm, whereas methine protons (-CH-) are found at about 1.5 ppm. Virtually all protons connected to a carbon bearing a heteroatom or functional group will resonate downfield of these signals

2. Electronegative atoms deshield the nucleus and the proton absorbs at low field (downfield). When the proton is connected to a carbon connected to oxygen, nitrogen, halogen, or sulfur, the bond polarization is such that the proton has less electron density and it is deshielded. That proton will appear downfield relative to methyl, methylene, and methine of an alkane. The more polarized the C-X bond, the further downfield the proton will appear.

3. Functional groups that are classified as electron withdrawing will deshield the nucleus and the proton will absorb at low field. Cyano groups, carbonyl-bearing functional groups, and nitro groups are all electron withdrawing since they have a $\delta+$ atom connected to the carbon bearing the proton of interest. This pulls electron density away from the proton, deshields it, and that signal will appear at lower field.

The carbonyl group shifts the signal downfield to about 2.1 ppm relative to methyl, and oxygen shifts the signal to about 3.3 ppm relative to methyl. Oxygen and the halogens also shift the signal downfield by similar amounts, and it can be difficult to distinguish these signals using only proton NMR

The C=C unit is clearly not as polarized as the carbonyl (C=O), so the alkene protons further downfield relative to the proton on a H-C-C=O unit. These are the α-protons on a ketone or an aldehyde, not the aldehyde hydrogen, O=C-H. Knowing that the alkyne proton is upfield of the alkene.

4. π Electrons have spin and, therefore, generate a magnetic field that opposes Ho. Just as sigma electrons generate a secondary field (have a magnetic moment), π-electrons also generate a secondary magnetic field that influences H_o. The greater the concentration of π -electrons, the greater will be the secondary magnetic field.

In this paper it has been explained experimentally the shielding and deshielding of proton in environment of chromium containing complex. Since the products obtained are complexes of chromium, and chromium is electron donating atom or ion therefore it may cause the deshielding and shift the signals into lower field.

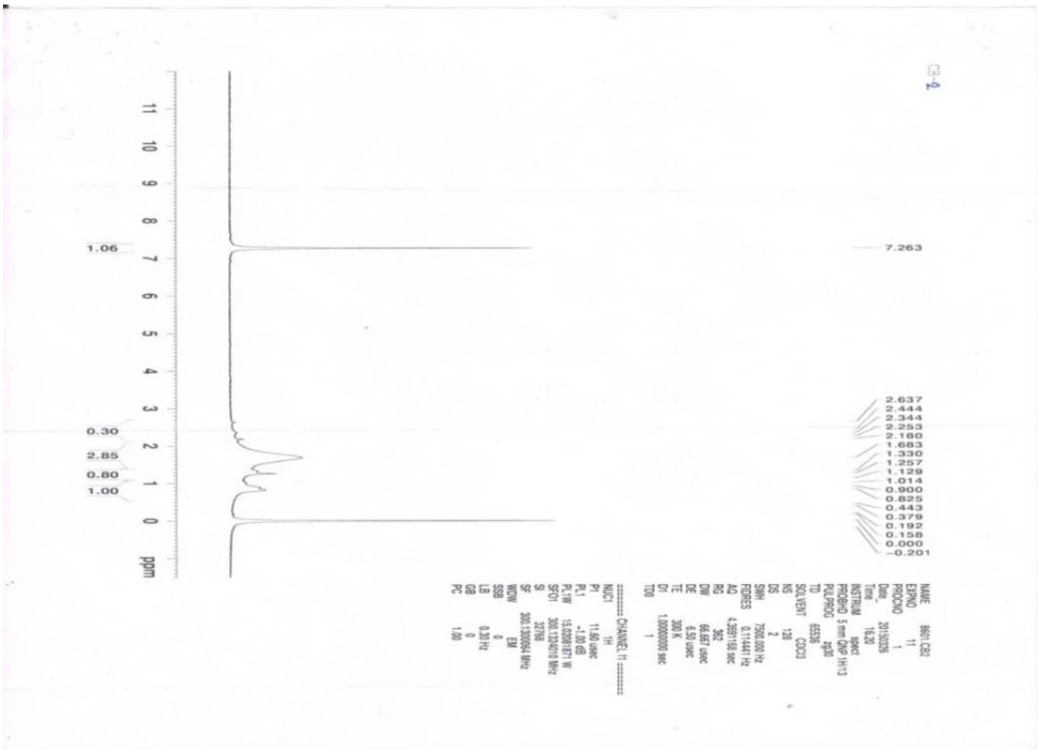
Experimental[6]:

a) **CB2:** Caproic acid was oxidized by TBC in molar ratio 1:0.75 (acid : TBC). The complex thus obtained was analysed by NMR spectral analysis.
b) **CB4:** Caproic acid was oxidized by TBC in molar ratio 1:1.25 (acid : TBC). The complex thus obtained was analysed by NMR spectral analysis.

c) **AB2:** Adipic acid was oxidized by TBC in molar ratio 1:0.75 (acid : TBC). The complex thus obtained was analysed by NMR spectral analysis.

d) **AB4:** Adipic acid was oxidized by TBC in molar ratio 1:1.25 (acid : TBC). The complex thus obtained was analysed by NMR spectral analysis **Result and discussion:**

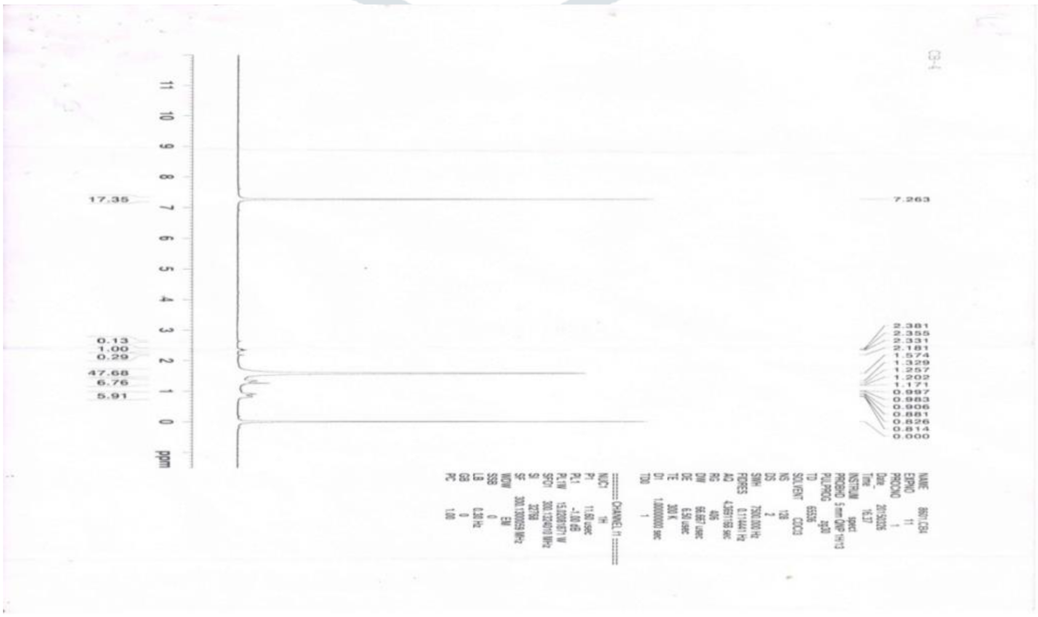
a) CB2: H NMR spectra of sample CB2



Groups identified on the basis of this spectra

δ in ppm	Type of proton
0.9	Primary (CH_3 or CH_2CH_3)
1.1	Primary (CH_3 or CH_2CH_3)
1.3	Secondary (-CH_2- or -CH_2CH_2-)
2.4	-OH
7.2	-CHO or -COOH

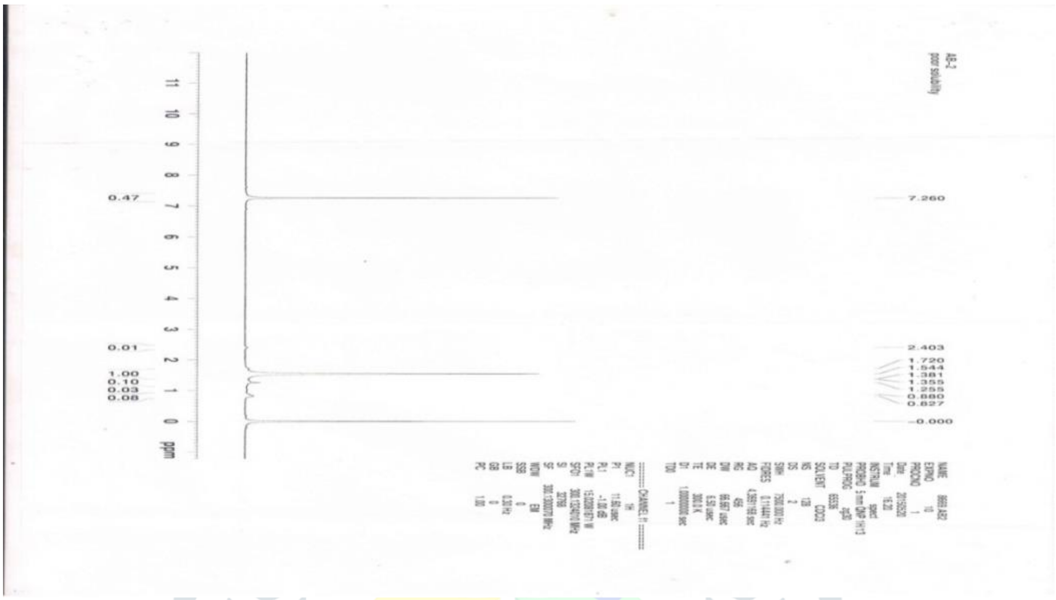
b) CB4: H NMR spectra of sample CB2



Protons identified on the basis of this spectra are following

δ in ppm	Type of proton
0.9	Primary (CH_3 or CH_2CH_3)
1.2	Primary (CH_3 or CH_2CH_3)
1.5	Secondary (-CH_2- or -CH_2CH_2-)
2.1, 2.3, 2.6	-OH
7.26	-CHO or -COOH

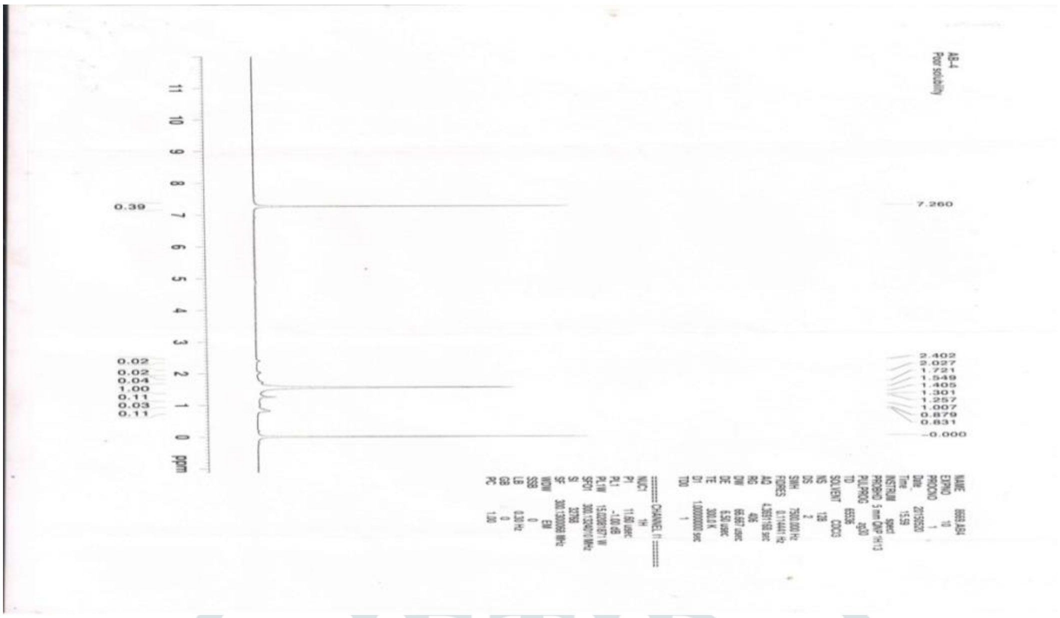
c) AB2 NMR Spectra:



Groups identified on the basis of this spectra are following

δ in ppm	Type of proton
0.827	Primary (CH_3 or CH_2CH_3)
0.880	Primary (CH_3 or CH_2CH_3)
1.225	Primary (CH_3 or CH_2CH_3)
1.54	Secondary or –CH2-CH2-
2.403	-OH
7.260	-CHO or -COOH

AB4 NMR Spectra:



Groups identified on the basis of this spectra are following

δ in ppm	Type of proton
0.879	Primary (CH_3 or CH_2CH_3)
1.0	Primary (CH_3 or CH_2CH_3)
1.25	Primary (CH_3 or CH_2CH_3)
1.5	Secondary or –CH2-CH2-
2.0	-OH
2.4	-OH
7.2	-CHO or -COOH

Conclusion: On the basis of this observation it can be explained that the presence of chromium in the environment of carboxylic or aldehydic proton reduces its chemical shift and the chemical shift identified for it are between 7.2 to 7.7. Presence of chromium may be cause for deshielding and signals are observed in lower field. Products obtained in this experiment are complexes of chromium and the metals are electron donating group therefore it causes deshielding ofproton. Hence signals are at lower field than the actual values. Some other groups identified in this observation are methyl (CH_3), methylene ($-CH_2-$), -OH etc. values of chemical shift of these protons are also affected by some extent due to shielding and deshielding.

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