

Determination of Stability Constants of N-[2-Hydroxy-5-Methylbenzylidene]-4-Carboxyaniline Complexes with Y³⁺, La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺ and Dy³⁺

M. S. MAYADEO and V. P. DHAKAPPA

Department of Chemistry, Ramnarain Ruia College, Matunga, Bombay-400 019

Manuscript received 19 September 1980, revised 23 March 1981, accepted 14 August 1981

IN the present communication the successive stability constants (log K₁ and log K₂) of the complexes of N-[2-hydroxy-5-methylbenzylidene]-4-carboxyaniline with various trivalent metal ions have been determined.

respectively. The protonation of the imino nitrogen probably does not take place as is observed from the titration curves.

The log K₁ and log K₂ values were calculated by least square method. The most representative values are recorded in Table 1. The order of stability of metal chelates was found to be Y³⁺ > Sm³⁺ > Dy³⁺ > Nd³⁺ > Gd³⁺ > Pr³⁺ > La³⁺.

Acknowledgement

The authors thank Dr. D. G. Vartak, B.A.R.C., Bombay, for valuable suggestions and Prof. A. P. Rao, Vice-Principal, Ramnarain Ruia College, Bombay, for kind and continuous encouragement.

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES*

Cations	t = 25°					μ = 0.1 M			
	H ⁺	Y ³⁺	La ³⁺	Pr ³⁺	Nd ³⁺	Sm ³⁺	Gd ³⁺	Dy ³⁺	
log K ₁	10.75	9.49	7.95	8.23	8.29	8.90	8.28	8.57	
log K ₂	7.65	7.99	7.43	7.55	7.82	7.85	7.66	7.77	

*For proton association (H⁺) K₁ and K₂ correspond to the species LH and LH₂⁺ respectively while for metal ions, K₁ and K₂ correspond to the species LM and L₂M respectively.

Experimental

The ligand N-(2-hydroxy-5-methylbenzylidene)-4-carboxyaniline was prepared by refluxing equimolar quantities of 5-methylsalicylaldehyde and *p*-aminobenzoic acid in methanol. The product was repeatedly crystallised to get an analytically pure compound (observed m.p. 258°).

All measurements were carried out at 25 ± 0.1°. The experimental details and computational methods were the same as described in earlier communications¹⁻⁴.

Results and Discussion

It may be stated here that the reagent does not undergo hydrolysis under the experimental conditions described. This was indicated by the rapid attainment of equilibrium and by the absence of any significant drift in pH meter readings even after one hour.

In the ligand it is the phenolic (OH) group which takes part in complex formation and the proton is replaced from it by the metal ion during chelation. Since only one proton per ligand molecule is liberated during complexation, 'Y', the number of dissociable protons attached to each ligand molecule is one.

The formation curve of \bar{n}_A versus B extends over a range of 0.21 < \bar{n}_A < 1.99 and is wave-like. From this curve pK^H , which corresponds to the association of proton to phenoxide ion of the reagent and pK^H_2 which corresponds to the association of proton to carboxylate ion of the reagent were obtained at $\bar{n}_A = 0.5$ and 1.5 respectively. These were further corroborated from the plots of

$$\log \left[\frac{\bar{n}_A}{1 - \bar{n}_A} \right] \text{ vs } B \text{ and } \log \left[\frac{2 - \bar{n}_A}{\bar{n}_A - 1} \right] \text{ vs } B$$

References

1. M. S. MAYADEO, A. M. CHAUBAL and S. D. VARTAK, *J. Indian Chem. Soc.*, 1978, 55, 450.
2. M. S. MAYADEO and V. P. DHAKAPPA, *J. Indian Chem. Soc.*, 1980, 57, 580.
3. M. S. MAYADEO and V. P. DHAKAPPA, *J. Indian Chem. Soc.*, 1980, 57, 849.
4. M. S. MAYADEO and V. S. PUROHIT, *J. Indian Chem. Soc.*, 1980, 57, 1047.

¹³C NMR Studies : Effect of Delocalization of Electrons on the Chemical Shift of Carbon Atoms in α -aryl- β -methyl cinnamonitriles*

MAHAVIR PRASHAD, M. SETH and A. P. BHADURI

Division of Medicinal Chemistry, Central Drug Research Institute, Lucknow-226 001

and

AVIJIT BANERJI**

Department of Pure Chemistry, University College of Science, Calcutta-700 009

Manuscript received 16 March 1981, accepted 14 August 1981

¹³C NMR spectra of saturated and unsaturated nitriles are interesting for more than one reason. For example, the saturated nitriles show a remarkably small α -effect while the unsaturated nitrile such as the geometrical isomers of crotononitrile exhibit different chemical shift of α - and β -carbon atoms¹. A trisubstituted- α , β -unsaturated nitrile in which the delocalization of electrons is influenced by

* CDRI Communication No. 2519

** To whom correspondence should be addressed.

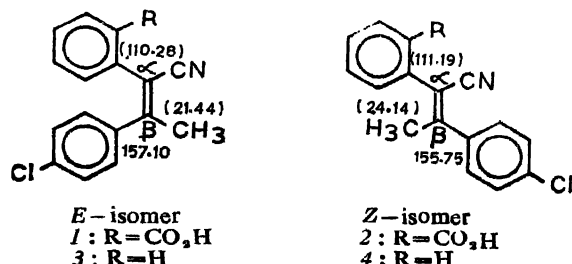
the stereochemistry of the molecule should, in principle, exhibit different chemical shifts of α - and β -carbons in the isomeric pair, but no attempt appears to have been made to ascertain the validity of this concept. This prompted the investigation of ^{13}C nmr spectra of α -aryl- β -methyl-4-chloro cinnamionitriles.

Experimental

The ^{13}C nmr spectra (noise-decoupled and off-resonance) were recorded on a Varian CFT-20 NMR spectrometer operating at 20.0 MHz in the Fourier-Transform mode using approximately one molar solutions in CDCl_3 at 22° . The spectra were obtained using pulses corresponding to tilt angles between 45° and 60° with a delay of 1.3–1.6 sec. between consecutive pulses. All the chemical shifts are expressed in δ ppm. The required compounds were obtained by the reaction of *o*-carboxy benzyl cyanide with *p*-chloro acetophenone³ and the geometrical isomers were separated by column chromatography over silica gel using CHCl_3 as the eluant.

Results and Discussion

The structure of α -aryl- β -methyl cinnamionitrile possesses a unique feature which permits the delocalization of electrons in both the geometrical isomers (3-4). In the *E*-isomer the delocalization of electrons occurs between the *p*-chlorophenyl ring and the cyano group and in the *Z*-isomer between the two aromatic rings.



However, a bulky substituent placed at the *ortho* position of the α -phenyl ring makes the situation different as is evident from the Dreiding model of 1 and 2. The steric interactions make the α -*o*-carboxyphenyl ring non-coplanar to the ethylenic bond in 1 and 2. In a situation such as this the delocalization of electrons between *p*-chlorophenyl ring and the cyano group in the *E*-isomer (1) remains undisturbed but in the *Z*-isomer (2) the flow of electrons between the two aromatic rings is hindered. The effect of delocalization of electrons, as would be evident from the chemical shift of α , β and methyl carbon atoms of 1 compared to those of 2 (Table 1) indicated the deshielding of the β -carbon and shielding of the α -carbon atom in 1. A plausible explanation for this observed effect is concerned with the ease of delocalization of π -electrons which renders the α -carbon atom of 1 to resonate at higher field and β -carbon atom at lower field as compared to those for the corresponding *Z*-isomer (2). This explanation is also in agreement with the one furnished by Stradi *et al.*². The resonance of the methyl carbons in 2 at lower field may possibly be explained on the

basis of the overall geometry of the molecule in which the electron pull by the cyano group contributes towards the observed effect. Comparative study of the chemical shifts of the nitrile carbon in 1-4 indicates that the difference of the chemical shifts is independent of the influence of the delocalization of electrons.

TABLE 1 - CHEMICAL SHIFTS OF VARIOUS CARBONS OF α -ARYL- β -METHYL-4-CHLORO CINNAMONITRILES

Compound No.	Isomer	α -C	β -C	CH_3	CN	CO_2H
1	<i>E</i>	110.28	157.10	21.44	121.57	171.88
2	<i>Z</i>	111.19	155.75	24.14	121.62	171.74
3	<i>E</i>	112.09	154.63	21.58	118.73	—
4	<i>Z</i>	112.32	154.49	21.74	118.90	—

The conclusion drawn from this study reveals that the steric interactions originating because of bulky *ortho*-substituents present in the geometrical isomers 1 and 2 make the delocalization of electrons between the *p*-chlorophenyl ring and the cyano group possible only in 1. This results in the shielding of the α -carbon and deshielding of the β -carbon in the *E*-isomer (1).

Acknowledgement

Sincere thanks are due to Dr. Y. P. Gavrilov of Shemyakin Institute of Bioorganic Chemistry, U.S.S.R. Academy of Sciences, Moscow for repeating the ^{13}C NMR spectra of a couple of compounds.

References

- J. B. STOTHERS, "Carbon-13 NMR spectroscopy", Academic Press, New York, 1972, p. 156.
- R. SIRADI, P. TRIMARCO and A. VIGEVANI, *J. Chem. Soc., Perkin I*, 1978, 1.
- M. PRASHAD and A. P. BHADURI, *Indian J. Chem.*, 1978, 16(B), 1058.

Chemical Investigation of the Leaves of *Aesculus indica*

M. K. BHATTACHARYA, P. K. GHOSH and K. S. MUKHERJEE*

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235, West Bengal

Manuscript received 28 November 1979, revised 24 March 1981, accepted 14 August 1981

AESCULUS indica (Family-Hippocastanaceae) is a large deciduous tree with a short, straight, cylindrical bole and a spreading crown with dropping branches. It is distributed from the Indus to Nepal, generally growing in rich, moist, shady ravines on the hill tops of Kashmir, the Punjab and Uttar Pradesh at an altitude of 4000–10000 ft. It is widely used as an indigenous drug^{1,2} in various ailments. The fruits are given to horses in colic. An oil from the seeds is used externally in rheumatic complaints. In this communication we

*To whom all correspondence may be made.