NMR Spectral correlations in some Tröger's bases

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ABSTRACT

Some Tröger's bases have been synthesised from substituted anilines and paraformaldehyde in presence of Lewis acid catalyst such as anhydrous AlCl_3 , through electrophilic substitution reaction. The purities of these Tröger's bases have been checked by their physical constants and spectroscopic data published earlier in the literature. The NMR chemical shift (δ , ppm) of methylene protons and carbon were assigned. The assigned methylene protons and carbon chemical shifts (δ , ppm) of synthesised Tröger's bases have been correlated with Hammett substituent constants, F and R parameters using single and multi-regression analyses. From the results of statistical analyses, the effects of substituent on methylene protons and carbon were discussed.

Keywords: Tröger's bases; NMR spectra; Hammett correlations; Substituent effects

1. INTRODUCTION

Tröger's base (Fig. 1), is a molecule containing chiral nitrogen centres exists in two enantiomeric form. Due to its rigid and concave shape, it has attracted an intense research in the last several decades [1]. Its chiral nature was first identified by Prelog and Wieland in 1944 [2]. Many Tröger's bases of the type whether substituted or condensed aromatic rings have been reported as 8H,16H-7,15-methanodinaphtho[2,1-b][2',1'-f][1,5]-diazocine, was synthesized by Tálas et al., [3]. Organic chemists synthesized various kinds of Tröger's base derivatives from C- amino heterocycles [4,5, naphthalimide fluorephore[6, rigid C_2 -symmetric crown ether [7], Chiral primary bis-ammonium salts [8], rearrangement of pyrazolines [9] mercaptanes [1], halogenation [10] and N-methyl pyrrole units [11,12]. The mechanism of formation of Tröger's base derivatives were investigated Abella et.al., [13] through AEI Mass spectral data. Chiral recognition by phenomena [14,15] was important for various fields likeracemic mixture resolution, determination of enantiomeric purity of chiral compounds and the selectivity of catalysts. Periasamy and Sathishkumar investigated the chiral recognition of carboxylic acids in the Tröger's base derivatives [14,15]. Several catalysts were employed for the synthesis of enantioselective rigid Tröger's base derivatives such as TiCl_4 , AlCl_3 , SnCl_4 , ZnCl_2 , ZrCl_4 [14], TFFA [16], Na_2CO_3 [17]. Didier and Sergeyev synthesized a few symmetrical amino and amino ethyl Tröger's base derivatives via Pd catalyzed C-C and C-N bond formation [18].

Fig. 1. General structure of Tröger's base.

Tröger's base derivatives are also used as catalysts for organic synthesis-construction of new supramolecular hosts [19,20], complexation [21], diastereoselective self-assembly of double standard helicates [21,23], molecular tweezers [24,25], scaffolds [26,27] and HPLC chromophoric solid phase supporters [28-30]. The synthesis of pure optically active Ru(II) complexes with a chiral Tröger's base ligands and their interaction towards DNA was investigated by Classens et al., [31]. DFT phenomena and NMR spectroscopy data were used for investigation of the various properties of Tröger's base derivatives [24]. Spectroscopic data is useful for prediction of ground state equilibration of molecules [32]. Generally compounds including Tröger's bases which are having hetero atom like O, S, N and notified functional group such as carbonyl, alkene, alkynes, halogens possess biological activities [33]. Herein, the authors wishes to report the synthesis of a series of enantioselective Tröger's base derivatives and studied the effects of substituent on methylene protons and carbons from their NMR chemical shifts(ppm) using single and multi-linear regression analysis.

2. EXPERIMENTAL

2. 1. Materials and methods

All chemicals used were purchased from Sigma-Aldrich and E-Merck chemical companies. Melting points of all Tröger's bases were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on AVATAR-300 Fourier transform spectrophotometer. The NMR spectra are recorded in INSTRUM AV500 NMR spectrometer, operating at 500 MHz for ^1H spectra and 125.46 MHz for ^{13}C spectra in CDCl_3 solvent using TMS as internal standard. Electron impact (EI) (70 eV) and FAB^+ mass spectra were recorded using VARIAN 500 mass spectrometer.

2. 2. General procedure for the synthesis of substituted Tröger's bases [33]

To an appropriate molar mass of substituted anilines (10 mmol) and paraformaldehyde (20 mmol) in CH_2Cl_2 (30 mL), anhydrous AlCl_3 (1.36 g, 10 mmol) was added under N_2 atmosphere. The reaction mixture was stirred for 12 h at 25 $^\circ\text{C}$ (Scheme 1) and quenched with cold water (10 mL). The reaction mixture was extracted with CH_2Cl_2 (20 mL) and the combined organic extracts were successively washed with water, brine and dried over

anhydrous Na_2SO_4 . After removal of the solvent, the residue was subjected to chromatography on alumina (basic) column using 10 % ethyl acetate in hexane to elute the desired Tröger's base analogs [14,15,33]. The analytical and Mass and NMR spectroscopic data are presented in Table 1.

Entry	R ₁	R ₂	R ₃	R ₄
1	H	H	H	H
2	H	H	NH ₂	H
3	Br	H	H	H
4	H	Br	H	H
5	H	H	Br	H
6	Cl	H	H	H
7	H	Cl	H	H
8	H	H	Cl	H
9	H	H	CN	H
10	F	H	H	H
11	H	F	H	H
12	H	H	F	H
13	H	H	OC ₂ H ₅	H
14	H	H	COOC ₂ H ₅	H
15	H	H	OCH ₃	H
16	H	H	CH ₃	H
17	H	H	NO ₂	H
18	H	H	CF ₃	H

Scheme 1. Synthesis of Tröger's bases

3. RESULTS AND DISCUSSION

3. 1. ^1H NMR spectral study

In the present study, the compounds chosen for evaluating the effects of substituents on methylene unit in Tröger's bases is shown in Scheme 1. The NMR spectra of synthesised Tröger's bases were recorded in CDCl_3 solvent using TMS as internal standard. The Chemical shifts (δ , ppm) of methylene protons and carbons of synthesised Tröger's bases were presented in Table 1. These chemical shifts(δ , ppm) have been correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis [32,34-44]. In this correlation the Hammett equation was taken in the form as

$$\delta = \rho\sigma + \delta_0 \quad \text{.....(1)}$$

where δ_0 is the frequency for the parent member of the series.

The results of statistical analyses of correlation of δHa and Hb chemical shifts (ppm) of Tröger's bases with Hammett substituent constants, F and R parameters were presented in Table 2. From Table 2, the correlation of δHa chemical shifts (ppm) values correlated satisfactorily with Hammett substituent constants and F parameters individually except NH_2 , 4- OCH_3 , 4- COOC_2H_5 , 4- NO_2 , 4-CN, 4- OC_2H_5 and 4-F substituents. The resonance parameter was failed in correlation with these frequencies. This is due to the lone pair of nitrogen atom opposes the effect of substituents on the methylene moiety and is associated with the resonance conjugative structure shown in Fig. 2. All correlations gave positive ρ values except σ_R constants and Resonance parameters.

Table 1. Physical constants, microanalysis mass (m/z) fragments and NMR chemical shifts (δ , ppm) of Tröger's bases.

Entry	M. F.	M. W.	M.p. ($^{\circ}\text{C}$)	Mass (m/z)	^1H NMR		^{13}C NMR
					Ha (1H, d)	Hb (1H, d)	δCH_2
1	$\text{C}_{15}\text{H}_{14}\text{N}_2$	222	131-132 (130-131) [33]	222[M^+]	4.065	4.117	66.721
2	$\text{C}_{15}\text{H}_{16}\text{N}_4$	252	267-268 (267-268) [33]	252[M^+]	4.601	4.760	66.632
3	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{Br}_2$	378	162-163 (162-163) [33]	378[M^+], 380[M^{2+}], 382[M^{4+}]	4.617	4.692	66.817
4	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{Br}_2$	378	203-204 (203-204) [33]	378[M^+], 380[M^{2+}], 382[M^{4+}]	4.671	4.690	66.714
5	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{Br}_2$	378	163-164 (163-164)	378[M^+], 380[M^{2+}],	4.217	4.276	67.010

			[33]	382[M ⁴⁺]			
6	C ₁₅ H ₁₂ N ₂ Cl ₂	290	144-145 (144-145) [33]	290[M ⁺], 292[M ²⁺], 294[M ⁴⁺]	4.678	4.680	66.825
7	C ₁₅ H ₁₂ N ₂ Cl ₂	290	192-193 (192-193) [33]	290[M ⁺], 292[M ²⁺], 294[M ⁴⁺]	4.680	4.687	66.619
8	C ₁₅ H ₁₂ N ₂ Cl ₂	290	144-145 (144-145) [33]	290[M ⁺], 292[M ²⁺], 294[M ⁴⁺]	4.301	4.367	67.117
9	C ₁₇ H ₁₂ N ₂	282	249-250 (249-250) [33]	282[M ⁺]	4.021	4.137	66.715
10	C ₁₅ H ₁₂ N ₂ F ₂	246	123-124 (123-124) [33]	246[M ⁺], 248[M ²⁺], 250[M ⁴⁺]	4.687	4.717	66.901
11	C ₁₅ H ₁₂ N ₂ F ₂	246	140-141 (140-141) [33]	246[M ⁺], 248[M ²⁺], 250[M ⁴⁺]	4.601	4.651	66.517
12	C ₁₅ H ₁₂ N ₂ F ₂	246	117-118 (117-118) [33]	246[M ⁺], 248[M ²⁺], 250[M ⁴⁺]	4.311	4.357	66.781
13	C ₁₉ H ₁₉ N ₂ O ₂	310	137-138 (137-138) [33]	310[M ⁺]	4.107	4.181	66.076
14	C ₂₁ H ₂₂ N ₂ O ₄	366	125-126 (125-126) [33]	366[M ⁺]	4.055	4.103	66.472
15	C ₁₇ H ₁₅ N ₂ O ₂	282	170-171 (170-171) [33]	282[M ⁺]	4.015	4.017	66.027
16	C ₁₇ H ₁₈ N ₂	250	136-137 (136-137) [33]	250[M ⁺]	4.101	4.137	66.173
17	C ₁₅ H ₁₂ N ₄ O ₄	274	256-257 (256-257) [33]	274[M ⁺]	4.192	4.271	67.217
18	C ₁₇ H ₁₂ N ₂ F ₆	316	129-130 (129-130) [33]	316[M ⁺], 318[M ²⁺], 320[M ⁴⁺]	4.176	4.192	66.817

Table 2. Results of statistical analysis of NMR chemical shifts (δ , ppm) of methylene protons and carbon of Tröger's bases with Hammett substituent constants, F and R parameters.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
Ha	σ	0.933	4.264	0.226	0.26	13	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃
	σ^+	0.943	4.269	0.213	0.24	13	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃
	σ_I	0.904	4.037	0.697	0.24	15	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-CF ₃
	σ_R	0.902	4.243	-0.305	0.24	14	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-COOC ₂ H ₅ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	F	0.900	4.403	0.649	0.23	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	R	0.811	4.355	-0.197	0.27	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
Hb	σ	0.926	4.316	0.191	0.25	13	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃
	σ^+	0.943	4.317	0.196	0.24	13	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃
	σ_I	0.848	4.098	0.657	0.23	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	σ_R	0.831	4.283	-0.330	0.25	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	F	0.905	4.103	0.620	0.22	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃

	R	0.824	4.294	-0.223	0.25	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
CH ₂	σ	0.964	66.519	0.632	0.38	15	H, 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	σ^+	0.905	66.581	0.322	0.31	17	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	σ_I	0.900	66.213	1.103	0.29	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-CH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	σ_R	0.836	66.748	0.535	0.34	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	F	0.849	66.332	0.758	0.31	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃
	R	0.836	66.756	0.461	0.33	18	H, 4-NH ₂ , 2-Br, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-CN, 2-F, 3-F, 4-F, 4-OC ₂ H ₅ , 4-COOC ₂ H ₅ , 4-OCH ₃ , 4-CH ₃ , 4-NO ₂ , 4-CF ₃

r = correlation coefficient, I = intercept, ρ = slope, s = standard deviation, n = number of correlated derivatives

This implies that there is a normal-substituent effects operates in all correlation. The correlation of δH_b chemical shifts (ppm) values correlated satisfactorily with Hammett σ , σ^+ substituent constants and F parameters individually except NH₂, 4-COOC₂H₅, 4-NO₂, 4-CN and 4-OC₂H₅ substituents.

Fig. 2. The resonance - conjugative structure.

If these substituents were included in the analysis, the result will be poor correlation. The remaining Hammett substituent constants and resonance parameters were fails in correlation. This is due to the inability of inductive and resonance effects of substituents on the methylene of all bases by opposing the lone pair of nitrogen atom and associated with the resonance conjugative structure shown in Fig. 2. The ratio of ρ_{Ha} and ρ_{Hb} is greater than 1 for σ and σ^+ . This implies that the transmittance of substituents effects on the methylene protons is higher extent for Ha chemical shifts(ppm) than Hb.

In single parameter regression analysis, some of the correlations of δ_{Ha} and Hb chemical shifts (ppm) of Tröger's bases were fails with some Hammett substituent constants, F and R values. While seeking the multi linear correlation, these frequencies correlated satisfactorily with Inductive, Resonance and Swain-Lupton's[44] constants collectively and the correlated equations are given in 2-5.

$$\delta_{\text{Ha}}^{(\text{ppm})} = 3.960 (\pm 0.137) + 0.717(\pm 0.295)\sigma_{\text{I}} - 0.334(\pm 0.238) \sigma_{\text{R}} \quad \dots(2)$$

$$(R = 0.957, n = 19, P > 95 \%)$$

$$\delta_{\text{Ha}}^{(\text{ppm})} = 4.022 (\pm 0.122) - 0.627(\pm 0.249)F - 0.119(\pm 0.020) R \quad \dots(3)$$

$$(R = 0.957, n = 19, P > 95 \%)$$

$$\delta_{\text{Hb}}^{(\text{ppm})} = 4.016 (\pm 0.130) + 0.679(\pm 0.280)\sigma_{\text{I}} - 0.357(\pm 0.226) \sigma_{\text{R}} \quad \dots(2)$$

$$(R = 0.958, n = 19, P > 95 \%)$$

$$\delta_{\text{Hb}}^{(\text{ppm})} = 4.071 (\pm 0.111) - 0.225(\pm 0.228)F - 0.577(\pm 0.235) R \quad \dots(3)$$

$$(R = 0.959, n = 19, P > 95 \%)$$

3. 2. ^{13}C NMR Spectral study

The Chemical shifts (δ , ppm) of methylene carbons of synthesised Tröger's bases were presented in Table 1. These chemical shifts (δ , ppm) have been correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis [32,34-44]. The results of statistical analysis are presented in Table 2. From the table 2, the methylene carbon chemical shifts (δ , ppm) of Tröger's bases with Hammett σ , σ^+ and σ_{I} constants were correlated satisfactorily. The remaining substituent constants, F and R parameters were failed in correlation. This is due to the reason stated earlier and associated with the resonance conjugative structure shown in Fig. 2. All correlation gave positive ρ values. This means that there is a normal substituent effect operates in all systems.

The correlations of methylene carbon chemical shifts (ppm) of Tröger's bases were fails with some Hammett substituent constants, F and R values in single parameter regression analysis. When seeking the multi linear regression, it is worthwhile that these frequencies correlated satisfactorily with Inductive, Resonance and Swain-Lupton's[44] constants collectively and the correlated equations are given in 6 and 7.

$$\delta_{\text{CH}_2}^{(\text{ppm})} = 66.325 (\pm 0.600) + 1.073(\pm 0.344)\sigma_{\text{I}} + 0.492(\pm 0.275) \sigma_{\text{R}} \quad \dots(2)$$

$$(R = 0.968, n = 19, P > 95 \%)$$

$$\delta_{\text{CH}_2}^{(\text{ppm})} = 66.432 (\pm 0.142) + 0.863(\pm 0.295)F + 0.574(\pm 0.243) R \quad \dots(3)$$

$$(R = 0.967, n = 19, P > 95 \%)$$

4. CONCLUSIONS

A series of Tröger's bases have been synthesized by electrophilic substitution reaction of substituted anilines and paraformaldehyde in presence Lewis acid catalyst anhydrous AlCl_3 . The purities of these Tröger's bases were checked by their physical constants and spectroscopic data published earlier in the literature. The NMR spectroscopic frequencies (δ , ppm) of methylene protons and carbons were assigned. The assigned chemical shifts (δ , ppm) of methylene protons and carbons have been correlated with Hammett substituent constants, F and R parameters using single and multi-regression analyses. From the results of statistical analyses, the effects of substituents on methylene protons and carbon were discussed.

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