

The Synthesis and Characterisation of a New Tröger's Base Content Methoxy Group

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ABSTRACT

Five Tröger's base (TB) molecules were synthesized by reaction aniline's derivatives which content a methoxy group with a supplement of methylene (dimethoxymethane (DMM)) in present trifluoroacetic acid (TFA) as a solvent and catalyst. This method afforded a good ratio product between 62% to 99%, all products were conforming by FTIR, HRMS, ¹HNMR, ¹³CNMR, and XRD.

Keywords: Tröger base, heterocyclic compounds, chirality

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INTRODUCTION

The first Tröger's base was create in 1887 by Julius Tröger during his Ph.D. studied, this compound was called Tröger base 1 (TB1) which from the condensation of methanal with 4-aminotoluene in HCl-catalysed media.¹ The TB1 (2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine) was conformed structure through chemical reaction by M. A. Spielman in 1935,² and then later through single crystal X-ray diffraction by S. B. Larson and C. S. Wilcox.³ The TB was described as "fascinating molecules"⁴⁻⁷ that because their structure of TB has a chiral 1,5-diazocine bridge locks contains double stereogenic nitrogen atoms in its rigid twisted V-shaped,⁸⁻¹⁰ as well as have two enantiomers of Tröger's base exists at room temperature.¹¹⁻¹² A many of functionalised enantiomers have been synthesized from suitably substituted amino-aryls and these compounds have been used in applications such as estimation of molecular,^{10,13-19} Deoxyribonucleic acid (DNA) binding studies,²⁰⁻²⁵ catalysis as molecules or polymers,²⁶⁻³¹ Subsequently, several Tröger bases polymer synthesised as thermal stability polymer,³² as ladder polymers for potential applications after casting membranes to gas separation³³⁻³⁹ or as network polymers.⁴⁰ In this work several analogues Tröger base substituted a methoxy group were formed and conformed by FTIR, ¹H-NMR, ¹³CNMR, Mass and XRD.

Experimental

General Procedure

An aniline derivative substituted a methoxy group was dissolved or suspended into dimethoxymethane (DMM) and the mixture was cooled in an ice bath. Trifluoroacetic acid (TFA) was added dropwise and the mixture could stir at room temperature for 24h. The mixture was slowly poured into aqueous ammonium hydroxide solution and stirred vigorously for 2 h during which a solid was formed. The solid was collected by filtration, washed with water and hexane until the washings were clear. The crude product was subjected to column chromatography (eluent: 8:2 hexane: dichloromethane) and the solvents were removed under vacuum. The product as a fine powder was

collected by filtration and was dried in a vacuum oven at 50 °C for 2 h.

1- Synthesis of 2,9-Dimethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5)diazocine (TB-OCH₃-1)

General procedure was followed using *m*-anisidine (9.1 ml, 10.00 g, 81.20 mmol), DMM (10.8 ml, 9.269 g, 121.80 mmol) and TFA (40 ml) to afforded (20.02 g, 87.33 %) as a brown powder. Mp = 193 - 195 °C; FTIR (solid, cm⁻¹) ν = 3206 cm⁻¹ (Ar-H), 2944 & 2839 cm⁻¹ (asy. str. & sy. str. of OCH₃ & CH₂ bridge), 1666, 1618 and 1498 cm⁻¹ (C=C of Ar), 1325 cm⁻¹ (Ar-N), 1197 cm⁻¹ (Caliph-N); ¹H NMR (500 MHz, CDCl₃) δ _H (ppm) = 7.88-6.93 (m, 6H, ArH), 4.45 (d, J = 16.90 Hz, 2H, alipha), 4.15 (s, 2H, alipha), 3.90 (d, J = 16.90 Hz, 2H, alipha), 3.70 (s, 6H, OCH₃); ¹³C NMR (126 MHz, CDCl₃) δ _C (ppm) = 156.3 (Ar), 147.0(Ar), 131.7(Ar), 120.0(Ar), 103.5(Ar), 99.8(Ar), 67.4(N-Calipha-N), 60.7(Ar-Calipha-N), 56.2(OCH₃); HRMS (EI, m/z): calculated 282.1362, found 282.1359 (M⁺).

2- Synthesis of 1,4,7,10-Tetramethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5) diazocine (TB-OCH₃-2)

General procedure was followed using 2,5-dimethoxyaniline (10.00 g, 65.28 mmol), DMM (8.7 ml, 7.452 g, 97.92 mmol) and TFA (40 ml) to afforded (15.48 g, 69.31 %) as a deep brown powder. Mp = 136 - 138 °C; FTIR (solid, cm⁻¹) ν = 2942, 2837, (asy. str. & sy. str. of OCH₃ & CH₂ bridge), 1688, 1626 & 1508 (C=C of Ar), 1350 cm⁻¹ (Ar-N), 1200 cm⁻¹ (Calipha-N); ¹H NMR (500 MHz, CDCl₃) δ _H (ppm) = 7.30 (d, J = 9.9 Hz, 2H, Ar), 6.97 (d, J = 9.9 Hz, 2H, Ar), 4.55 (d, J = 13.0 Hz, 2H, alipha), 4.02 (s, 2H, alipha), 3.78 (d, J = 13.0 Hz, 2H, alipha), 3.72 (s, 12H, OCH₃); ¹³C NMR (126 MHz, CDCl₃) δ _C (ppm) = 152.1 (Ar), 140.1(Ar), 131.2(Ar), 115.2(Ar), 108.6(Ar), 104.8(Ar), 67.5(N-Calipha-N), 56.2(OCH₃), 50.7(Ar-Calipha-N); HRMS (EI, m/z): calculated 342.1574, found 342.1562 (M⁺).

3- Synthesis of 1,3,8,10-Tetramethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5) diazocine (TB-OCH₃-3)

General procedure was followed using 2,4-dimethoxyaniline (9.3 ml, 10.00 g, 65.28 mmol), DMM (8.7 ml, 7.452 g, 97.92 mmol) and TFA (40 ml) to afforded (14.02 g, 62.72 %) as a brown powder. Mp = 94 - 96 °C;

FTIR (solid, cm^{-1}) $\nu=2935, 2843$, (asy. str. & sy. str. of OCH_3 & CH_2 bridge), $1690, 1637$ & 1508 ($\text{C}=\text{C}$ of Ar), 1450 cm^{-1} (Ar-N), 1200 cm^{-1} (Caliphatic-N); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{H} (ppm) = 6.03 (Ar), 5.90 (Ar), 4.65 (d, $J = 12.4$ Hz, 2H, alipha), 4.32 (s, 2H, alipha), 4.00 (d, $J = 12.4$ Hz, 2H, alipha), 3.75 (s, 12H, OCH_3); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ_{C} (ppm) = 150.1 (Ar), 145.8(Ar), 125.2(Ar), 123.9(Ar), 107.7(Ar), 100.2(Ar), 67.6(N-Calipha-N), 60.7(Ar-Caliph-N), 56.2(OCH_3); HRMS (EI, m/z): calculated 342.1574, found 342.1565 (M^+).

4-1,10-Dimethoxy-4,7-dimethyl-6H,12H-5,11-methanodibenzo[b,f](1,5)diazocine (TB-OCH₃-4)

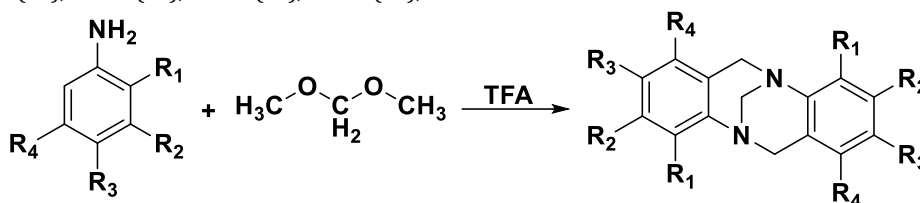
General procedure was followed using 2-methoxy-5-methylaniline (10.00 g, 72.90 mmol), DMM (9.7 ml, 8.321 g, 109.35 mmol) and TFA (40 ml) to afforded (22.50 g, 99.43 %) as a yellow powder. Mp = 125 - 127 °C; FTIR (solid, cm^{-1}) $\nu=3032, 2942, 1664, 1566, 1462, 1375, 1197$; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{H} (ppm) = 6.30 (d, $J = 19.3$ Hz, 2H, Ar), 6.12 (d, $J = 19.3$ Hz, 2H, Ar), 4.98 (d, $J = 10.1$ Hz, 2H, alipha), 4.33 (s, 2H, alipha), 3.57 (d, $J = 10.1$ Hz, 2H, alipha), 3.70 (s, 12H, OCH_3); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ_{C} (ppm) = 142.5 (Ar), 131.9(Ar), 130.2(Ar), 124.7(Ar), 120.6(Ar),

114.8(Ar), 67.1(N-Calipha-N), 56.0(OCH_3), 53.7(Ar-Caliph-N), 17.9(Caliph); HRMS (EI, m/z): calculated 310.3972, found 310.3955 (M^+).

5- Synthesis of 1,10-Dimethoxy-4,7-dinitro-6H,12H-5,11-methanodibenzo[b,f](1,5) diazocine (TB-OCH₃-5)

General procedure was followed using 2-methoxy-5-nitroaniline (10.00 g, 59.47 mmol), DMM (8.0 ml, 6.789 g, 89.21 mmol) and TFA (40 ml) to afforded (16.40 g, 74.06 %) as a yellow powder. Mp = 128 - 130 °C; FTIR (solid, cm^{-1}) $\nu=3096, 2978, 2943, 1660, 1620, 1577, 1510$ (asy. NO_2 , 1334 sy. NO_2 , 1264; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ_{H} (ppm) = 7.30 (d, $J = 22.9$ Hz, 2H, Ar), 6.67 (d, $J = 22.9$ Hz, 2H, Ar), 4.70 (d, $J = 17.2$ Hz, 2H, alipha), 4.22 (s, 2H, alipha), 3.89 (d, $J = 17.2$ Hz, 2H, alipha), 3.70 (s, 12H, OCH_3); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ_{C} (ppm) = 151.7 (Ar), 142.1(Ar), 130.5(Ar), 118.2(Ar), 115.0(Ar), 111.1(Ar), 67.3(N-Calipha-N), 56.1(OCH_3), 50.5(Ar-Caliph-N); HRMS (EI, m/z): calculated 372.1064, found 372.1059 (M^+).

Reactions equation of synthesis Tröger base



No. of compound	R ₁	R ₂	R ₃	R ₄	Yield (%)	Code
1	H	OCH ₃	H	H	87.30	TB-OCH ₃ -1
2	OCH ₃	H	H	OCH ₃	62.72	TB-OCH ₃ -2
3	OCH ₃	H	OCH ₃	H	62.74	TB-OCH ₃ -3
4	OCH ₃	H	H	CH ₃	99.43	TB-OCH ₃ -4
5	OCH ₃	H	H	NO ₂	74.06	TB-OCH ₃ -5

Results and Discussion

A Tröger base was synthesised according to patent⁴¹ with modification by reaction of aniline's derivatives dimethoxymethane (DMM) which is a "methylene" source in a strongly acidic solvent and catalyst like trifluoroacetic acid (TFA). A typical procedure of reaction is one equivalent of a pure aromatic amine is mixed with two and half equivalents of dimethoxymethane (DMM) and cooled to ice temperature. TFA (4-5 ml per gram of amine) is then slowly added dropwise over ten minutes. The reaction mixture is stirred at room temperature under a constant inert atmosphere for 24h. The colour of the solution will be change to a brown or black colour. Aqueous ammonium hydroxide solution was used to quench the mixture by slowly poured the reaction mixture to precipitate the afforded product as a solid. The products are filtered and washed with water to remove any inorganic waste and then hexane. The crude product was exhibited to column chromatography (eluent: 8:2 hexane: DCM) and the solvents were removed under vacuum. The product as a fine powder was collected by filtration and was dried in a vacuum oven.

One of the evidences to form our compounds the FTIR, which showing the tertiary amine peak while the primary

amine peaks is disappear. As well as the Caliph-N peak was show near 1200 cm^{-1} , based to some other group like NO_2 . $^1\text{HNMR}$ refers to Ar-N- CH_2 for Tröger bases cyclic at $\delta \sim 5$ and ~ 4 ppm beside to N- CH_2 -N between $\sim \delta 4.4$ ppm. $^{13}\text{CNMR}$ of Tröger bases refers to $\text{C}_{\text{Ar}}-\text{O}-\text{CH}_3$ δ 141-152 ppm, $\text{C}_{\text{Ar}}-\text{N}$ at δ 147-141 ppm and Calipha-N at $\delta \sim 67$ and 50.5-60.7 ppm, beside to methoxy group ~ 56 ppm. Structural analysis of the Five Tröger's base (TB) molecules has been achieved using the X-ray diffraction (XRD) as shown in Figure (1). The XRD patterns of all composites show that the synthesis molecules have polycrystalline nanostructure. As shown in the figure, the methoxy groups TB-OCH₃-1 composite has three notable peaks at (17.76° , 18.62° and 27.8°) of high intensity of preferred plane at (17.76°). The crystallite size (D) of all composites has been measured using the formula of Scherrer [1].

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the incident Cu K α radiation wavelength ($\lambda = 1.5406 \text{ \AA}$), β is the full width at half maximum (FWHM), and θ is the diffraction angle. The crystallite size value of preferred plane of SAK14 is found to be (70.8 nm). The addition of NO_2 to methoxy groups TB-OCH₃-1 led to create another group TB-OCH₃-5 composite of preferred

orientations at (11.03°, 22.09°, and 26.2°) with higher intensity at (26.2°). The calculated crystallite size value of preferred plane of SAK15 is (51.6 nm). This value indicates that the addition also reduces the crystallite size of methoxy groups. X-ray diffraction pattern confirms that the crystalline structure of TB-OCH₃-4 composite has been orientated at (44°, 64.34° and 77.5°) and is preferentially orientated along crystallographic plane of diffraction angle (44°) more than the other planes. The crystallite size value of preferred plane of SAK8 is found to be (60.5 nm). As replacing the methoxy group location in TB-OCH₃-4, the

intensity of the preferred orientation at (44°) is reduced and the preferred orientation becomes at (64.34°) with high intensity to give another composite TB-OCH₃-3. With another replacement of methoxy group location in TB-OCH₃-4, the preferred orientation at (44°) is continuously reduced to lower intensity than at TB-OCH₃-2 and get another composite SAK10 of the same preferred orientation at (64.34°) of TB-OCH₃-2. As a result, to replacement of methoxy group in TB-OCH₃-4, the crystallite sizes have been increased to be (63 nm) and (75.6 nm) of TB-OCH₃-2 and TB-OCH₃-3 respectively.

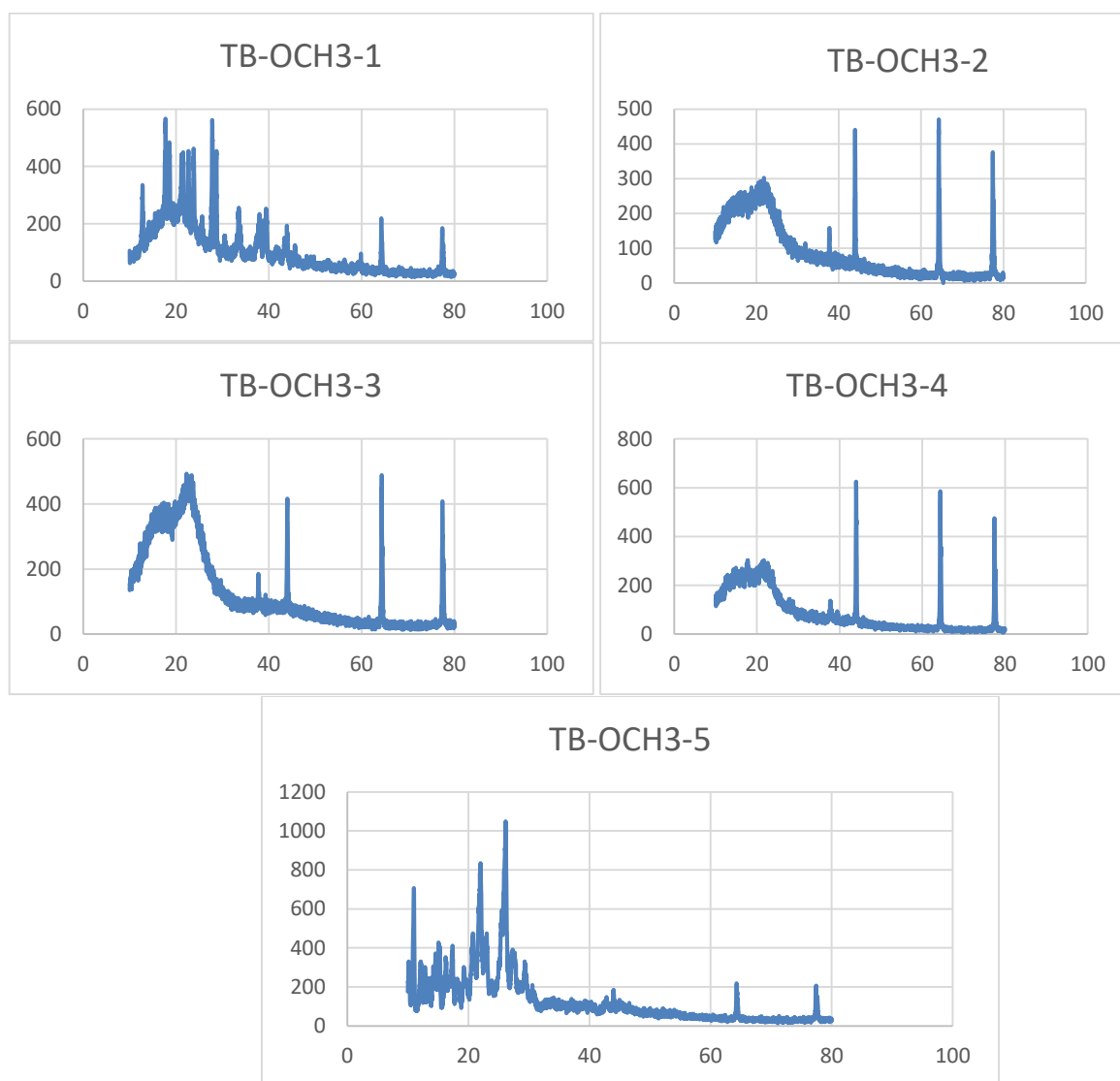


Figure 1. XRD of Tröger's base

2,9-dimethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5) diazocine compound multi crystalline with three top peaks and high intensity because the diffraction which contain three angles at (17.76°, 18.62° and 27.8°), respectively. Both a higher intensity and direction will be angle at 17.76°, by Scherrer equation (eq.1) to find the crystalline volume. The average of crystalline volume of directions was 70.8nm.

$$\tau = \frac{(K\lambda)}{\beta \cos \theta} \dots \text{eq.1}$$

Where:

τ : is a size of the ordered (crystalline) domains; K : is a dimensionless shape factor; λ : X-ray wavelength; β : is the

line broadening at half the maximum intensity (FWHM); θ : the Bragg angle.

When Tröger base has four substituted, so the result will be different. A compound 1,10-dimethoxy-4,7-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5)diazocine was multi crystalline with three top peak and high intensity at angles 44°, 63.34° and 77.5° but the best direction at 44° comparing with compounds 1,4,7,10-tetramethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5)diazocine and 1,3,8,10-tetramethoxy-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5)diazocine because the methyl group was a smaller than methoxy group. Furthermore, the change of methoxy position of Tröger base led to decreasing of

crystalline volume due to change of a higher intensity. Wherever the crystalline volume (60.5, 63 and 75.6) nm, respectively. A 1,10-dimethoxy-4,7-dinitro-6*H*,12*H*-5,11-methanodibenzo[*b,f*](1,5) diazocine compound showing a multi crystalline was a better direction at 11.03°, 22.09° and 26.2° angles but the higher was 26.2°. The Scherrer equation prove this compound is a Nano compound which the average crystalline volume was 51.6nm. The decreasing of average crystalline volume attributed to the nitro group.

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