

Novel organic crystals as candidates for frequency up-converted materials: syntheses and crystal structures of two Tröger's bases[†]

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The syntheses and crystal structures of two novel Tröger's bases as candidates for frequency up-converted organic materials are reported.

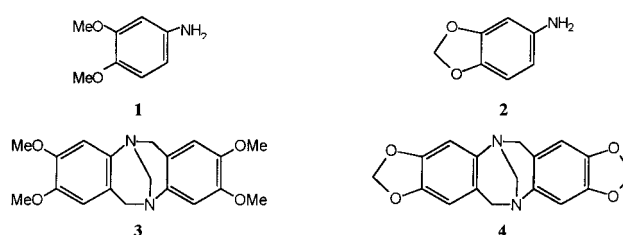
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Tröger's base, firstly reported by Tröger in 1887,¹ is a rigid and concave chiral molecule which could easily be obtained by acid-promoted condensation of *p*-aniline and formaldehyde. Historically, it was the first amine compound proven to have a rate of configurational inversion slow enough to allow resolution into its enantiomeric components.² Recently, Tröger's bases have been described as "fascinating molecules"³ due to their particular features present in their structure in which the chiral 1,5-diazocine bridge locks two aromatic rings in almost perpendicular planes. Some analogues of Tröger's bases containing crown-ether,⁴ porphyrin,⁵ 1,10-phenanthroline,⁶ and electron-withdrawing heterocycles⁷ have been synthesized and attracted attention of chemists in the areas of molecular recognition,⁸ DNA-interacting probes,⁹ catalytic hydrosilylation of alkynes¹⁰ and biomimetic systems.¹¹

The syntheses of the analogues of Tröger's bases are hampered by the special electronic requirement of the aniline in the condensation reaction. It is of interest to find new aniline derivatives that can be condensed and give access to new molecules with other interesting functionality. Recently, we found that they have frequency up-converted properties in the crystal state,¹² which is also a rare example for organic crystals to have frequency up-converted properties for short-wavelength compact lasers. We report herein the syntheses, crystal structures of two new Tröger's bases.

Reaction of aniline **1** or **2** with formaldehyde under acidic conditions afforded product **3** or **4**, respectively, in good yields (Scheme 1). Theoretically, the reaction may give rise to three different geometrical isomers: one with linear symmetry, one symmetric and one unsymmetrical. The ¹H NMR spectra of the products revealed only two aromatic singlets, clearly indicating that only **3** or **4** was formed.

The crystal structures of both compounds (Fig. 1) were determined in order to study the influence of the replacement of six-membered benzene ring. Concerning the main aspect of the "armature" of Tröger's bases, *i.e.* the dihedral angle between the aromatic rings, these lie in the range of 88.6–104.1° reported by Wilcox *et al.*¹³ In this work, the dihedral angles are 99.1° for **3** and 85.0° for **4**, respectively. No significant differences in the "armature" are found, indicating



Scheme 1

that the eight-membered rings in the Tröger's bases are considerably flexible. In the crystal structure, we can see only one product with linear symmetry which is consistent with the NMR data. The molecular packing diagrams of **3** and **4** are shown in Fig. 2. For **3**, there are weak intermolecular C–H...O (N) hydrogen bonds and significant face-to-face π - π stacking interactions (each two neighbouring benzene rings in the dimer are parallel and separated by 3.014 Å) to form a dimer between the adjacent molecules in the unit cell; for **4**, weak C–H...O hydrogen bonds and π - π interactions between the parallel aromatic rings (separation: 3.958 Å) are also found to form a quasi-2-D stacking which stabilises the structure.

Experimental

Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The mass spectra were recorded on a PE SCIEX API-300 spectrometer. ¹H NMR spectra were recorded on a Bruker AC-P 500 spectrometer (200 MHz) with tetramethylsilane as the internal reference. All the reagents and solvents for syntheses and analyses were of analytical grade.

Preparation of 3 and 4: To a mixture of substituted aniline (5.0 mmol) in 37% formalin solution (5 ml) cooled to 0°C, concentrated HCl (4 ml) was then added dropwise and the solution was stirred at room temperature under Ar for *ca* 24 h. The volume of the reaction mixture was reduced to half under reduced pressure at 40–50°C and then poured into a 500 ml separatory funnel containing 150 ml H₂O and 10 ml NH₃·H₂O. The resulting mixture was then extracted by three portions of CH₂Cl₂ (70 ml each). Organic phases were combined and washed with 200 ml saturated NaHCO₃ solution and 200 ml saturated NaCl solution. The organic layer was dried over MgSO₄ and filtered. The solvent was removed under reduced pressure, and the residual material was recrystallized from CH₂Cl₂/MeOH to obtain colourless crystals suitable for X-ray analysis in high yield (80% for **3** and 75% for **4**). Selected data for **3**: ¹H-NMR (500 MHz, CDCl₃) δ 3.88 (s, 6H, Ar–OCH₃), 3.92 (s, 6H, Ar–OCH₃), 4.07 (d, *J* = 16.4 Hz, 2H, Ar–CH₂–N), 4.28 (s, 2H, N–CH₂–N), 4.61 (d, *J* = 16.4 Hz, 2H, Ar–CH₂–N), 6.38 (s, 2H, Ar–H), 6.66 (s, 2H, Ar–H); Exact Mass

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

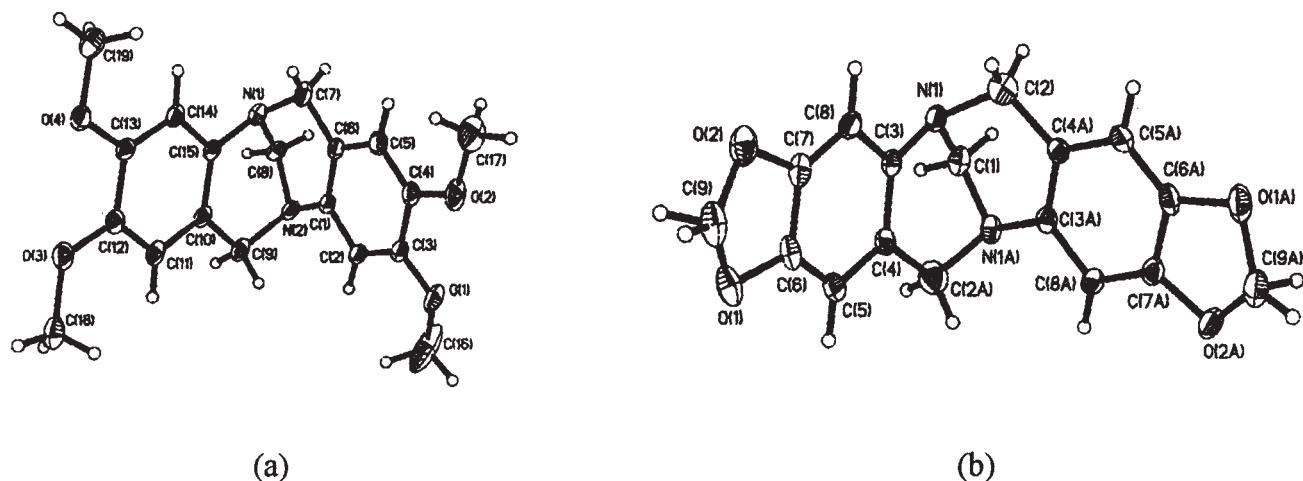


Fig. 1 The ORTEP structure of (a) 3; (b) 4.

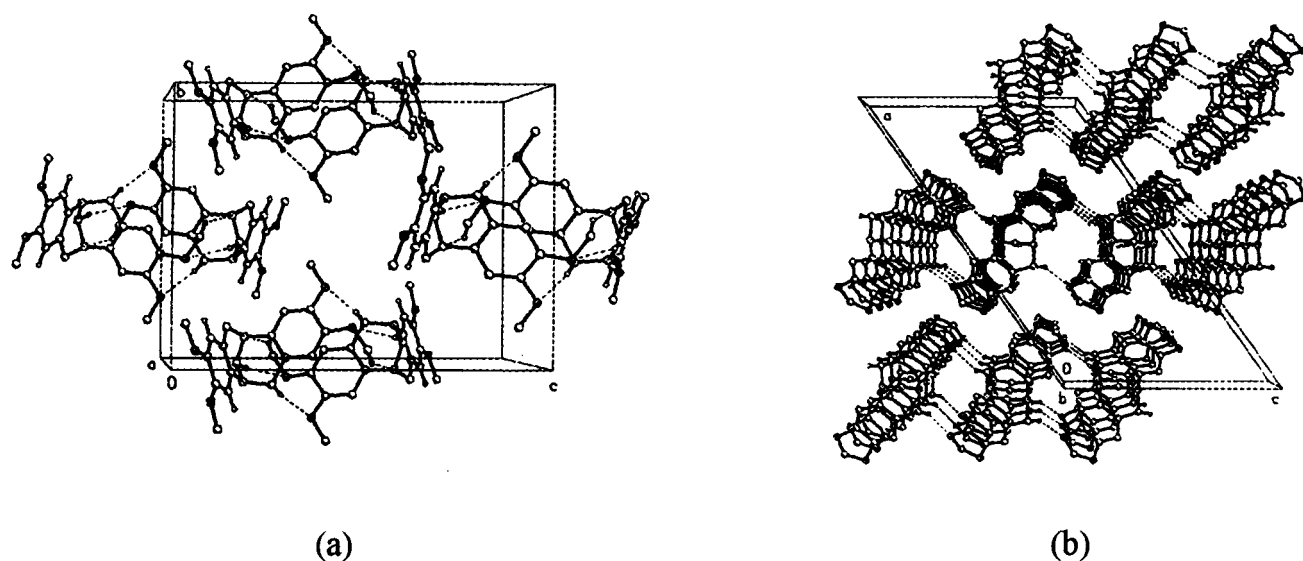


Fig. 2 Packing diagrams of (a) 3; (b) 4. Important hydrogen bond distances (Å) and angles (°): for 3, C(8)...O(3) 3.171, C(9)...O(4) 3.394, C(18)...N(1) 3.225; C(8)-H(8A)...O(3) 129.5, C(9)-H(9A)...O(4) 166.4, C(18)-H(18B)...N(1) 140.5; for 4, C(2)...O(2) 3.398, C(2)-H(2A)...O(2) 154.7.

calcd for $C_{19}H_{22}N_2O_4$: 342.39, Found: 342.16; Anal. Calcd for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18, Found: C, 66.62; H, 6.64; N, 8.14. For 4: 1N -NMR (400 MHz, $CDCl_3$) δ 3.99 (s, 2H, O-CH₂-O), 4.05 (s, 2H, O-CH₂-O), 4.63 (s, 2H, N-CH₂-N), 5.88 (d, $J = 2.0$ Hz, 2H, Ar-CH₂-N), 5.91 (d, $J = 1.6$ Hz, 2H, Ar-CH₂-N), 6.38 (s, 2H, Ar-H), 6.72 (s, 2H, Ar-H); Exact Mass calcd for $C_{17}H_{14}N_2O_4$: 310.30, Found: 310.04; Anal. Calcd for $C_{17}H_{14}N_2O_4$: C, 65.80; H, 4.55; N, 9.03, Found: C, 65.74; H, 4.58; N, 8.87.

X-ray analyses: Single crystal X-ray diffraction measurements were carried out with a Siemens CCD (for 3) or a Bruker Smart 1000 CCD (for 4) X-ray diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) at 298 K. Both structures were solved by direct methods and using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Crystal data for 3: $C_{19}H_{22}N_2O_4$, $M_r = 342.39$, monoclinic, space group $P2_1/c$, $a = 7.986(1)$, $b = 12.656(2)$, $c = 17.163(3)$ Å, $B = 99.12(1)^\circ$, $V = 1712.8(4)$ Å³, $Z = 4$, $D_c = 1.328$ g.cm⁻³, μ (Mo-K α) = 0.094 mm⁻¹, $F(000) = 728$. A total of 3532 reflections were collected and the independent reflection number is 2835 with 227 refined parameters ($R_{int} = 0.049$). Final convergent [$I \geq 2\sigma(I)$] $R = 0.058$, $wR = 0.075$ and Goodness-of-fit = 1.618. For 4: $C_{17}H_{14}N_2O_4$, $M_r = 310.30$, monoclinic, space group $C2/c$, $a = 22.587(5)$, $b = 5.3699(11)$, $c = 13.941(3)$ Å, $B = 126.097(3)^\circ$, $V = 1366.3(5)$ Å³, $Z = 4$, $D_c = 1.508$ g.cm⁻³, μ (Mo-K α) = 0.121 mm⁻¹, $F(000) = 648$. Final convergent [$I \geq 2\sigma(I)$]

$R = 0.0428$, $wR = 0.01247$ and $S = 0.974$ for 931 observed reflections and 106 refined parameters. Full crystallographic details will be deposited at the Cambridge Crystallographic data Centre (CCDC).

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