

A bow-phase mesogen showing strong, robust analog electro-optics^{1†}

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The design and synthesis of the first of a new class of bow-phase (also known as banana-phase) mesogens possessing resorcyldiene aniline groups in the core is described. The new achiral material, **NORABOW**, shows two chiral electro-optically active smectic phases, both existing over a wide temperature range. The high temperature smectic, which exists as the thermodynamically stable phase between 120 °C and 150 °C, exhibits electro-optic behavior not previously reported for a bow-phase. In particular, high susceptibility analog electro-optics (“V-shaped switching”) are observed in a texture which is stable to large applied electric fields. The electro-optic behavior of **NORABOW** is of potential utility in photonic switching applications.

1. Introduction

In a structural evolution paralleling that of the calamitic SmC* LCs, most bent-core (banana-shaped, or bow-shaped) mesogens² exhibiting the remarkable SmCP antiferroelectric³ and ferroelectric⁴ phases are Schiff bases. These bow-phase materials have recently been the subject of intense physical investigation.² But, as for the early SmC* materials, physical studies can be complicated by the hydrolytic instability of the molecules. While SmCP mesogens without Schiff base units have been reported,⁵ variations on the theme of the bis-Schiff base bent-core system have proven remarkably useful for providing interesting polar smectics.

The resorcyldiene aniline core, present in such classic calamitic FLCs as the MBRA⁶ and MORA⁷ series, actually seems superior to the benzylidene aniline core with respect to mesogenicity, and is more stable towards hydrolysis. This core also played a key role in the first discovery of antiferroelectrics from achiral molecules, being the core present in the pioneering Soto-Bustamante/Blinov anticlinic bilayer antiferroelectrics (SmAP_A).⁸ Since anticlinic layer interfaces are important for obtaining ferroelectric bow-phases, the Soto-Bustamante/Blinov result reinforces the idea that this structural feature may prove interesting when incorporated into bow-phase mesogens.

Given the enhanced stability and excellent mesogenicity of the resorcyldiene aniline core, we proceeded to explore this modification to the classic bow-phase mesogen structure. As described below, this effort has led to a new achiral electro-optically active bow-phase material exhibiting potentially useful high strength analog electro-optics in standard LC cells (V-shaped switching).

2. Synthesis and liquid crystalline texture of the new bow-phase mesogen **NORABOW**

To keep the structure close to that of the well-characterized Schiff base mesogens exhibiting SmCP phases, but also to

provide a straightforward synthesis, the target bis-*p*-NonylOxy-Resorcyldiene Aniline **3** was prepared as shown in Fig. 1. In keeping with the trivial nomenclature first suggested by the Chalmers group,⁷ we name this core unit “**NORA**”, and dub the new bent-core liquid crystal **NORABOW**. In this structure the Schiff base units in the core are “flipped” relative to their orientation in the classic bis-nonyloxybenzylideneamine Schiff base material **NOBOW** (structure and phase transitions are given in Fig. 1 for comparison). As we have previously reported, **NOBOW** exhibits the antiferroelectric SmC_SP_A macroscopic racemate as the thermodynamic phase, and the SmC_AP_A macroscopic conglomerate as a metastable phase easily obtained upon melting of the B4 “blue crystal” phase.^{4b}

Upon cooling of **NORABOW** from the isotropic liquid between the plates of a transparent capacitor test cell,⁹ a smectic focal conic liquid crystal texture develops at 145 °C, as seen in the polarized light microscope (Fig. 2). The texture is reminiscent of the B2 bow-phase texture, with the apparent formation of two distinct types of focal conic domains (isotropic regions are still present in this image). Domains of type A have a green birefringence color and are “SmA-like”, *i.e.* the optic axis is along the layer normal. Domains of type B have a pink birefringence color, and exhibit a tilt of the optic axis from the layer normal of about ±20°. No changes in the texture occur upon further cooling.

3. Electro-optics of **NORABOW**

Application of small electric fields (<2 V μm⁻¹) to a **NORABOW** cell evidences additional complexity and structural information not seen in the initial textures. First, a distinct analog rotation of the extinction brushes in the tilted domains of type B can be seen with application of the field. The response appears to be quite unsymmetrical (*i.e.* there is more rotation for one sign of the field than for the other), but domains of opposite tilt direction can be easily seen. This behavior proves that the tilted domains of type B are chiral, and that the sample is a conglomerate, containing domains of opposite handedness.

Interestingly, domains of type A, exhibiting the green birefringence color, occur in two distinctly different variations,

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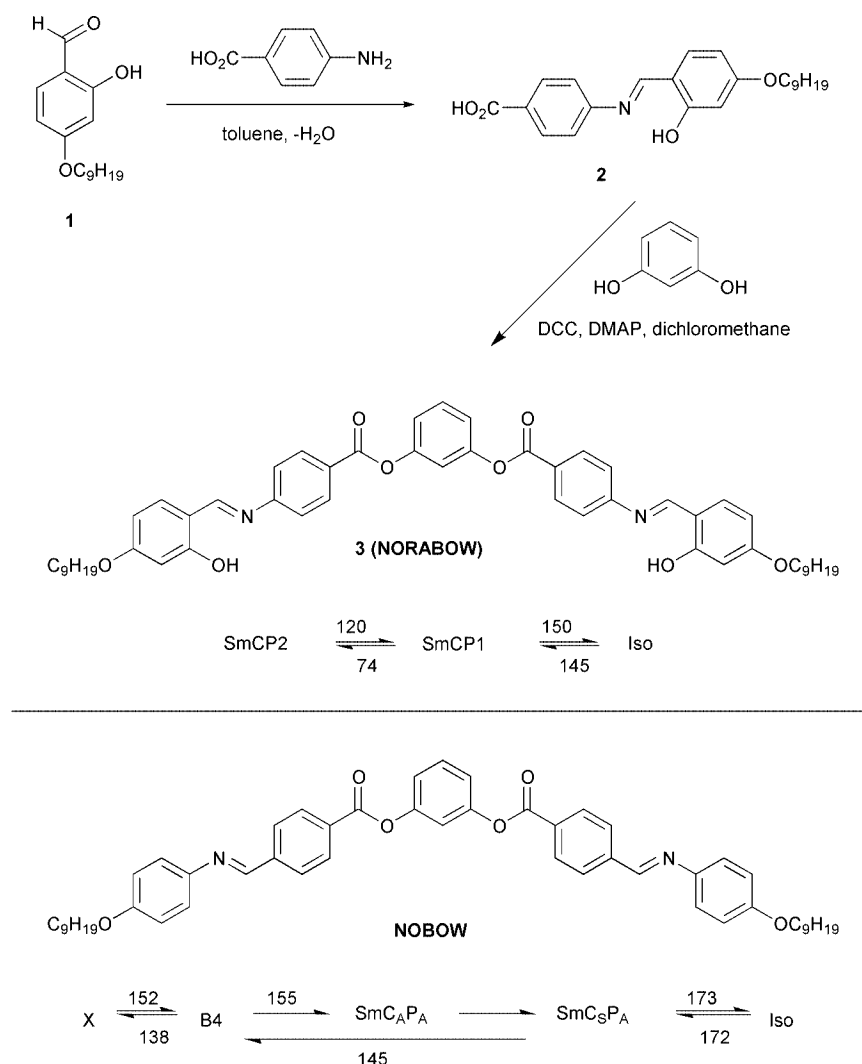


Fig. 1 The structure, synthesis, and transition temperatures of compound 3 (**NORABOW**) (temperatures are in degrees centigrade). The structure, phases and transition temperatures of the classic bow-phase mesogen **NOBOW** are also shown for comparison.

as indicated in Fig. 3. In one variety (labeled A2 in the figure), there is no brush rotation nor other visible electro-optic behavior at all upon application of a small field. In a second variety (A1) of these green “SmA-like” domains a complex change in texture occurs, where thin stripes appear parallel to the layers in the focal conics, as can be seen in Fig. 3. This response is quite easily seen, but there is no visible macroscopic brush rotation in the domains, and the response seems achiral.

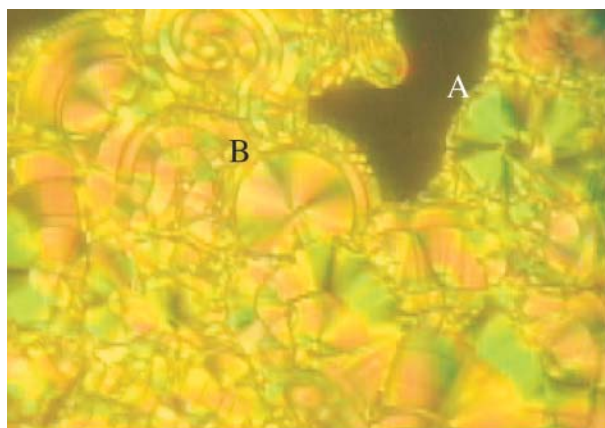


Fig. 2 Liquid crystal texture observed by polarized light microscopy (polarizer vertical, analyzer horizontal) upon cooling of **NORABOW** from the isotropic melt. This sample has not been exposed to an electric field.

At temperatures between 145 °C and 120 °C, upon application of a large field ($6 \text{ V } \mu\text{m}^{-1}$), the texture changes dramatically. Removal of the field then gives a smooth SmA-like focal conic texture (domains of type C) with a second order pink birefringence color, as shown in Fig. 4 ($E=0$). All of the initially formed domains of type A and type B change to this new texture upon application of the field then removal of the field. This texture is also obtained if the sample is cooled from the isotropic liquid phase in the presence of a field.

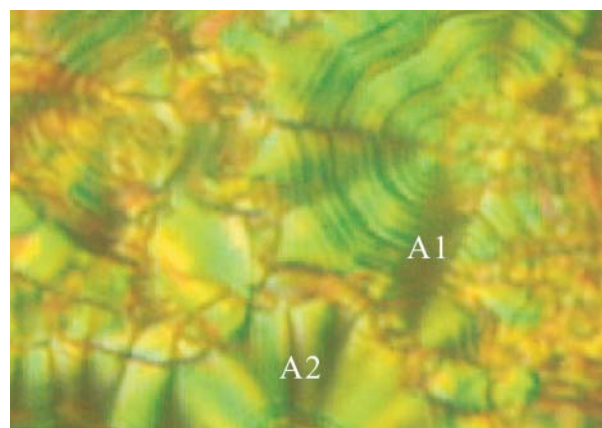


Fig. 3 Focal conic domains of type A with application of a small ($< 5 \text{ V } \mu\text{m}^{-1}$) electric field.

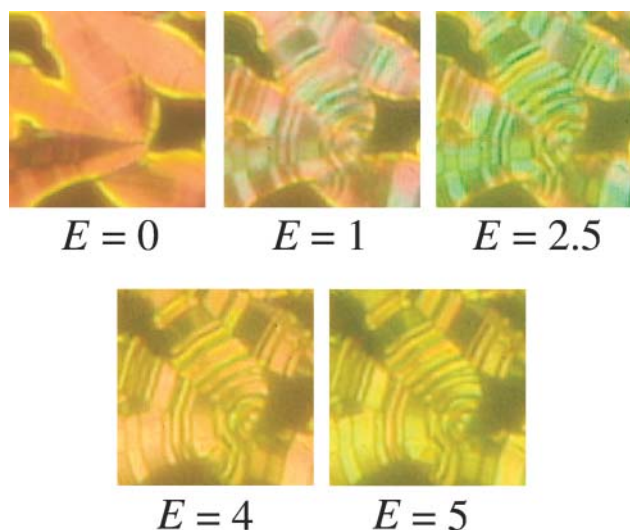


Fig. 4 Focal conic domains of type C obtained from **NORABOW** after application of a field above $6 \text{ V } \mu\text{m}^{-1}$ (fields indicated are $\text{V } \mu\text{m}^{-1}$).

The new texture changes dramatically upon application of a field. As can be seen in Fig. 4, thick stripes appear in the focal conic domains parallel to the layers, and the birefringence color changes quite dramatically. Upon progressing from zero field to an applied field of $5 \text{ V } \mu\text{m}^{-1}$, the birefringence color progresses in a continuous and reversible way through purple, blue, green, salmon, and finally a light yellow color in Newton's third order.

When the sample is driven with a triangular driving waveform centered about zero volts, it can be easily seen that the stripes appearing in the focal conic domains represent counter-rotating extinction brushes from chiral domains of opposite handedness. That is, the seemingly uniform focal conic domains are actually conglomerates with walls between heterochiral domains. These walls are invisible at zero applied field, but become visible as the brushes in the domains counter-rotate as the field increases.

Fig. 5 shows an area of the cell where cylindrical focal conic domains of opposite handedness can be seen. The counter-rotating nature of the brushes in these domains is very obvious when observing the cell's response to a triangular driving waveform. The rotation of the optic axis in these domains is quite large; $\sim \pm 35^\circ$, saturating at about $5 \text{ V } \mu\text{m}^{-1}$. The change

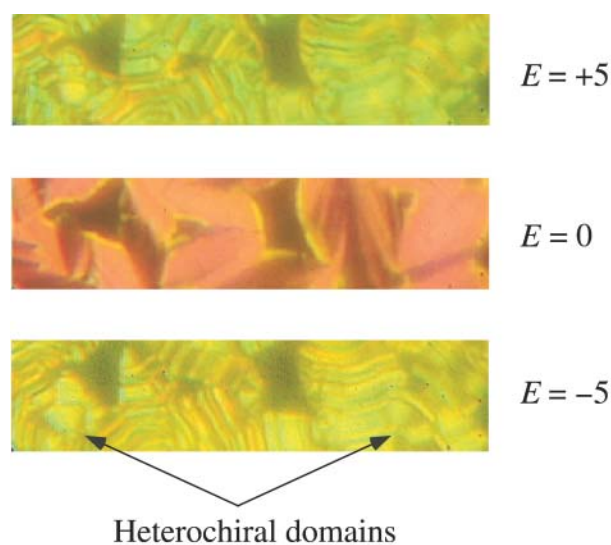


Fig. 5 Switching of heterochiral domains of type C showing the large saturation rotation of the optic axis at fields of $5 \text{ V } \mu\text{m}^{-1}$.

in optic axis orientation is analog, with no hint of a threshold as would be expected for an antiferroelectric.

Upon cooling the sample below 74°C a dramatic change in the electro-optic susceptibility of the system occurs, but with no change in the zero field texture. This new phase, SmCP2, shows a higher birefringence ($\Delta n^*d = 1600 \text{ nm}$; green birefringence color) than that of SmCP1 of type C at zero field, and the birefringence change and brush rotation in response to applied fields is smaller, but still easily observable. The SmCP2 phase is restored when the sample is heated to 120°C .

4. Discussion

While much work remains to be done to develop an understanding of the structure and electro-optics of the **NORABOW** SmCP phases, several features of the system deserve comment. First, it is interesting that none of the textures formed on cooling from the isotropic phase (focal conics of type A1, A2 and B) is similar to that obtained upon application of a field (either during formation of the texture or afterwards); focal conics of type C. Since domains of type C have never been seen to “relax” to another texture, we feel it is likely that this texture represents an alignment of the thermodynamic phase of the material. Textures of type A1, A2, and B are then either metastable phases (this often occurs with bow-phase materials), or different alignment modes of the thermodynamic phase, or some of both.

Second, the magnitude of the analog electro-optic response (~ 7 degrees/ $\text{V } \mu\text{m}^{-1}$) is similar to the largest electroclinic effect observed to date for a SmA* material,¹⁰ though not as large as the coefficients observed for “V-shaped switching” SmC* materials.¹¹ Even so, the electro-optic behavior of **NORABOW** is interesting in the context of potential applications of the bow-phases. While analog electro-optics have been reported for the SmC₅P_F bow-phase of the racemic **MHOBOW** in the low birefringence “gold focal conic” B7 texture,^{4a,12} in that case the analog susceptibility is small (~ 1 degree/ $\text{V } \mu\text{m}^{-1}$), and the texture changes irreversibly to a high birefringence “bistable blue” SSFLC-like alignment at high field. The bistable texture is also produced when this B7 material is cooled from the isotropic phase in the presence of a field.

We have proposed a mechanism for the analog electro-optics exhibited by **MHOBOW** and the change to bistable switching,^{4a} as illustrated in Fig. 6. In this scenario, the low-birefringence gold focal conic domains derive from “steric” alignment where the bow-plane is parallel to the substrate surfaces, forcing the layers and polarization to tilt from the surface normal (Fig. 6A). This alignment is identical to that of the “Sony mode” analog switch developed for calamitic SmC* materials.¹³ Application of electric fields along the substrate

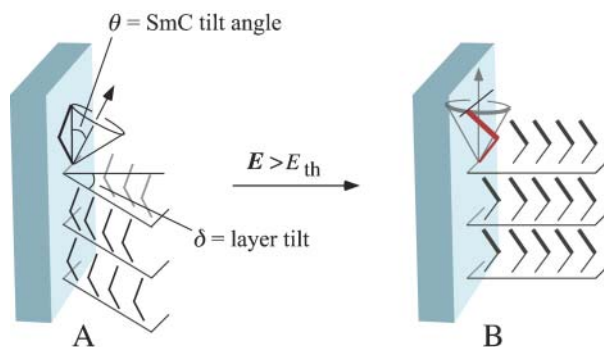


Fig. 6 Illustration of the proposed alignment modes for V-shaped analog switching (A) and bistable switching (B) in the SmC₅P_F bow-phase.

normal causes an analog rotation of the director on the (tilted) tilt cone.

In this alignment mode, however, the polarization cannot orient parallel to the applied field. If the field passes a threshold value, then the layers “straighten” in a manner similar to the formation of quasi-bookshelf alignment obtained when a large field is applied to a chevron SSFLC cell, such that the polarization can orient parallel to the field (6B). Bistable switching is then observed for this “bookshelf” alignment.

This mechanism is inconsistent with our observations concerning **NORABOW** electro-optics, however. In the case of **NORABOW**, the analog alignment is obtained when the sample is cooled from the isotropic phase in the presence of a field. This certainly implies that the analog switching is occurring in an alignment where the polarization (either induced or spontaneous) is parallel to the field at high fields. At this stage the behavior of **NORABOW** is, not surprisingly, mysterious. Some possible interpretations are: 1) the phase is antiferroelectric with a very low threshold and almost no hysteresis; 2) the phase is a SmA showing electroclinic switching into an induced SmC_SP_F; 3) the phase is a ferroelectric SmC_SP_F with high polarization and small screening from ions, providing electrostatically driven V-shaped switching analogous to that observed in SmC* materials;¹⁴ or 4) the layers (and tilt cone) are tilted when the polarization is parallel to the field, that is, the phase is a SmC_G,¹⁵ and there is strong biaxial anchoring preferring the bow plane parallel to the substrates.

5. Conclusions

In conclusion, a new bow-phase mesogen possessing a bis-resorcyldene aniline core, and showing a novel chiral, electro-optically active bow-phase, has been synthesized. The electro-optic behavior is especially interesting, showing a high susceptibility analog response to applied fields, with a large change in birefringence on tilting of the optic axis. These properties are of potential utility in a variety of photonic switching applications.

6. Experimental

NMR spectra were obtained with a Varian VXR-300S spectrometer (300 MHz) or with a Varian VXR-500 spectrometer (500 MHz). Spectra were referenced to CHCl₃ (7.24 ppm for ¹H, 77.0 ppm for ¹³C). Liquid crystal phases and phase transitions were determined using polarized light microscopy with a Nikon Optiphot2 POL microscope equipped with an INSTEC temperature controlled hot stage.

Dichloromethane was dried by distillation from CaH. Dry dimethylformamide (DMF), 2,4-dihydroxybenzaldehyde, 4-aminobenzoic acid, resorcinol, dicyclohexylcarbodiimide, 4-dimethylaminopyridine, 95% sodium hydride (NaH), and 1-bromononane were used as supplied from Aldrich Chemical Company.

2-Hydroxy-4-nonyloxybenzaldehyde (1)

To a solution of 2,4-dihydroxybenzaldehyde (15 g, 0.109 mol) in DMF (90 mL), cooled to 0 °C, was added 95% NaH (3.28 g, 0.130 mol). The reaction mixture was allowed to stir at room temperature for 1 h, then 1-bromononane (27 g, 25 mL, 0.130 mol) was added dropwise. The resulting mixture was allowed to stir overnight, then poured into 210 mL of water, and acidified to pH 3 with 5% aqueous HCl. This mixture was shaken with ether, and the organic layer was separated, washed with water and brine, then dried over MgSO₄. The crude product obtained after evaporation of solvent was purified by flash chromatography on silica gel using hexane–25% ethyl acetate as eluent. Known aldehyde **1** was obtained 8.5 g

(30%): ¹H NMR (300 MHz, CDCl₃) δ: 11.48 (1H, s, CH=O), 9.70 (1H, s, OH), 7.33 (1H, d, *J*=8.55 Hz, Ar), 6.52 (1H, d, *J*=10.99 Hz, Ar), 6.40 (1H, s, Ar), 4.00 (2H, t, *J*=6.59 Hz, OCH₂), 1.83–1.23 (14H, m, 7 CH₂), 0.89 (3H, t, CH₃).

4-(2-Hydroxy-4-nonyloxybenzylideneamino)benzoic acid (2)

To a solution of aldehyde **1** (3.28 g, 0.012 mol) in toluene (190 mL) was added 4-aminobenzoic acid (1.70 g, 0.012 mol), and the resulting mixture was refluxed for 24 h using a Dean–Stark trap for azeotropic removal of water. After cooling, the product (2.85 g) crystallized from the solution and was isolated by filtration. The resulting solid was washed with hexane and recrystallized from absolute ethanol to provide 2.58 g (56%) of acid **2**: ¹H NMR (500 MHz, d₇-DMF) δ: 8.98 (1H, s, CH), 8.09 (2H, d, *J*=8.52, Ar), 7.60 (1H, d, *J*=8.72 Hz, Ar), 7.52 (2H, d, *J*=8.32, Ar), 6.61 (1H, d, *J*=10.90 Hz, Ar), 6.53 (1H, s, Ar), 4.09 (2H, t, *J*=6.54, OCH₂), 3.50 (1H, br s, OH), 1.78–1.26 (14H, m, 7 CH₂), 0.86 (3H, t, CH₃); ¹³C NMR (500 MHz, d₇-DMF) δ: 167.68, 165.09, 164.79, 164.48, 153.05, 135.35, 131.59, 129.49, 122.02, 113.89, 108.19, 101.99, 68.88, 32.36, 26.46, 23.11, 14.27. MS (*m/z*): theor.: 383.2089; EI 383.3. EA for C₂₃H₂₉NO₄ (383.49) calculated: C 72.04%, H 7.62%, N 3.65%; found: C 72.13%, H 7.91%, N 3.61%.

1,3-Phenylene bis[4-(2-hydroxy-4-nonyloxybenzylideneamino)benzoate] (3)

To a solution of resorcinol (0.880 g, 0.008 mol) and acid **2** (1.15 g, 0.003 mol) in dichloromethane (110 mL) were added dicyclohexylcarbodiimide (0.742 g, 0.0036 mol) and 4-dimethylaminopyridine (20 mg). The resulting reaction mixture was stirred at room temperature for 48 h. The urea which formed during the reaction was removed by filtration and the dichloromethane was evaporated *in vacuo*. The solid residue was purified by flash chromatography on silica gel using dichloromethane–2% methanol as eluent and then crystallized from ethyl acetate, from absolute ethanol, and again from ethyl acetate, providing 170 mg (13%) of the target liquid crystal **3** as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ: 8.87 (2H, s, 2CH), 8.24 (4H, d, *J*=8.54, Ar), 7.50 (1H, t, *J*=8.24, Ar), 7.36–7.18 (9H, m, Ar), 6.50 (4H, s, Ar), 4.01 (4H, t, *J*=6.55 Hz, 2 OCH₂), 1.83–1.28 (28H, m, 14 CH₂), 0.89 (6H, t, 2 CH₃), 0.37 (2H, br s, 2 OH); ¹³C NMR (500 MHz, CDCl₃) δ: 164.37, 164.29, 164.09, 163.12, 153.36, 151.46, 134.02, 131.72, 129.87, 126.73, 121.26, 119.24, 115.85, 112.74, 108.11, 101.52, 68.36, 31.87, 29.51, 29.35, 29.25, 29.04, 25.97, 22.67, 14.11; MS (*m/z*): theor.: 840.4350, electrospray positive 841, exact mass found: 840.4381; EA for C₅₂H₆₀N₂O₈ (841.06) calculated: C 74.26%, H 7.19%, N 3.33%; found: C 73.84%, H 7.13%, N 3.28%.

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