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Asymmetric synthesis of a highly soluble 'trimeric' analogue of the chiral nematic liquid crystal twist agent Merck S1011

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The Sharpless asymmetric dihydroxylation has been utilised to synthesise a new glassy chiral dopant with large helical twisting power (β) and remarkable solubility in nematic liquid crystal hosts. Values of β range between +30.7 and +47.7 μm^{-1} in five different nematic hosts. A 26% mixture in E7 is homogenous indefinitely and induces a room-temperature blue phase.

Keywords: helical twisting power; chiral nematic; blue phase

1. Introduction

Calamitic liquid crystals (LCs) are anisotropic organic fluids consisting of rod-shaped molecules [1]. The simplest of the calamitic LC phases is the nematic phase wherein molecules self-organise with their long axes roughly parallel, thus having directional order but no positional order. When enantiomerically enriched chiral molecules ('twist agents') are doped into achiral nematic phases the molecules adopt a supramolecular helical ordering with the helix axis orthogonal to the molecular long axis. These chiral nematic (N*) phases are by far the most technologically exploited of the calamitics and are now ubiquitous in LC displays [2]. In a newly emerging technology, the flexoelectrooptic effect in short-pitch N* materials can also be employed to create LC displays [3]. The helical periodicity in the N* phase can also be exploited to create photonic band gap materials. Indeed, lasing from dye-doped chiral nematic LCs is another emerging field [4]. When helical pitch becomes very small (i.e. less than about 0.5 μm), three-dimensional cubic phases, called blue phases, can occur just above the temperature of the N* phase [5]. These tightly twisted chiral phases are attracting renewed attention and have also been used as photonic crystals [6]. Thus, there is currently great interest in soluble N* twist agents that can induce tight helical pitch at low concentrations.

The propensity of an enantiomeric molecule to induce helicity in the nematic phase is called helical twisting power (HTP or β) and is defined as

$$\beta = \frac{1}{p \cdot c \cdot r} \tag{1}$$

where p is the helical pitch in μm, c is the weight percent of dopant and r is the enantiomeric excess [7]. The sign of β defines the handedness of the N* helix and is related to (but not predicted by) the absolute stereoconfiguration of the enantiomeric dopant. Many twist agents with large HTP have been reported, including axially chiral biaryls [8, 9], Seebach's TADDOL ligands [10], and esters of chiral diols and sugars [11]. While dopants with large HTP are now available, many suffer from low solubility in nematic hosts. Therefore, multiple chiral dopants are often required to create short-pitch N* materials. One such modestly soluble N* twist agent is Merck S1011, first synthesised by Heppke and co-workers [12] shown in Figure 1.

Previously, we demonstrated that structural modifications to S1011 can have significant affects on HTP [13]. While efficient at inducing helicity, S1011 precipitates from the nematic host E7 at about 4% doping. Following the adage 'like dissolves like', the general strategy for increasing the solubility of LC dopants is often to make them structurally similar to the LC host. Indeed, we view S1011 as a 'dimer' structure comprising two mesogenic units (*trans*-4-pentyl-4′-cyclohexylbenzoic acid) joined by a chiral diol. We proposed that converting the central phenyl ring of S1011 ring into a third *trans*-4-pentylcyclohexyl mesogenic unit would increase HTP and/or solubility of the dopant. Scheme 1 illustrates our synthetic route for this structural elaboration of S1011 to give the 'trimeric' twist agent **RD2**.

2. Experimental

2.1 Materials

Reagent grade ethylene glycol, sodium hydroxide, hydrochloric acid, sulphuric acid, dichloromethane, tetrahydrofuran (THF), hexanes, ethyl acetate, diethyl

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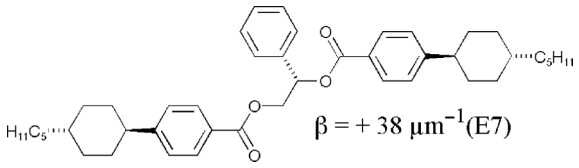


Figure 1. Merck S1011 (71 × 21 mm^2, 300 × 300 dpi^2).

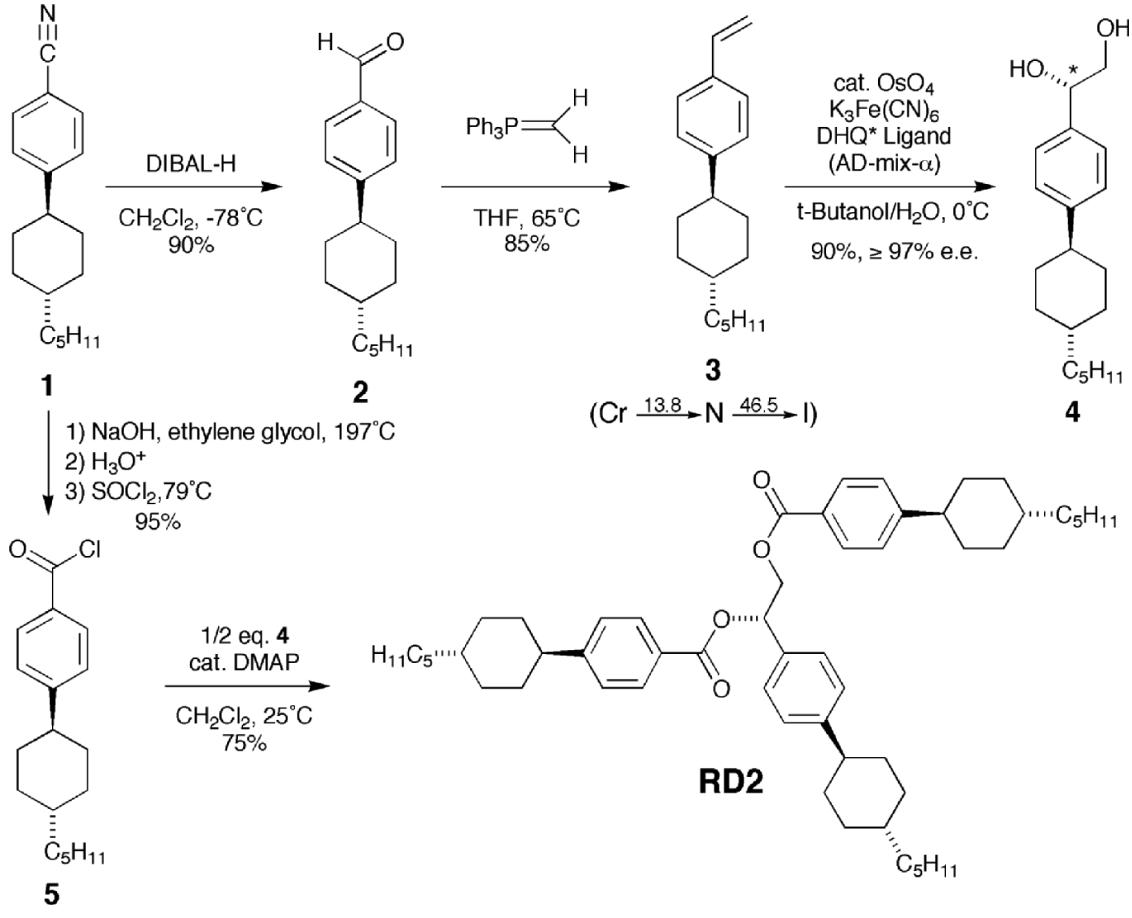
ether, *tert*-butanol and sodium sulphite were all obtained from Fisher Scientific and used as received. Solvents were stored over 3 Å molecular sieves. 4′-(4-*trans*-pentylcyclohexyl)benzonitrile, 1 M diisobutylaluminiumhydride in dichloromethane, methyltriphenylphosphonium bromide, 1.6 M n-butyllithium in hexanes, AD-mix-α, 4-(dimethylamino)pyridine, (R)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (Mosher's acid), 1-phenyl-1,2-ethanediol, (S)-(+)-1-phenyl-1,2-ethanediol, triethylamine, thionyl chloride, N,N'-dicyclohexylcarbodiimide, and 1-hydroxybenzotriazole were all obtained from Sigma-Aldrich and used as received. Nuclear magnetic resonance (NMR) spectra of synthetic products were obtained on a Varian 300 MHz Gemini spectrometer. NMR spectra of Mosher esters of chiral diols were obtained on a Bruker Avance 400 MHz spectrometer.

Nematic hosts E7 and ZLI2806 were obtained from Merck (Darmstadt, Germany) and used as received. 4′-pentyl-4-biphenylcarbonitrile (5CB) and 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CyITC) were obtained from Sigma-Aldrich and used as received.

2.2 *Synthesis of RD2*

2.2.1 *4′-(4-trans-pentylcyclohexyl)benzoic acid (**2**)*

4′-(4-*trans*-pentylcyclohexyl)benzonitrile, 5.0 g (19.6 mmol), was suspended in 250 ml ethylene glycol. Sodium hydroxide, 7.8 g (196 mmol), was added at room temperature. The mixture was brought to reflux at which time reagents were dissolved in the now amber solution. Immediately after achieving reflux, a colourless floating precipitate formed. The heterogeneous mixture was stirred at reflux for 18 h. The mixture was cooled to room temperature and poured



Scheme 1. Synthesis of a trimeric analogue of S1011 (179 × 145 mm^2, 300 × 300 dpi^2).

into 500 ml 1 M HCl. The resulting solid was filtered and recrystallised from ethanol to give 5.0 g of colourless needles (93%). m.p. 152–155°C; ^{1}H NMR (300 MHz, CDCl3) δ 0.88 (t, J = 6.2 Hz, 3H), 1.02 (m, 2H), 1.25 (m, 9H), 1.44 (m, 2H), 1.87 (m, 4H), 2.52 (tt, J = 12.6, 3.5 Hz, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 14.1, 22.7, 26.6, 32.2, 33.4, 34.0, 37.2, 37.3, 44.8, 126.8, 127.0, 130.3, 154.3, 171.2.

2.2.2 *4′-(trans-4-pentylcyclohexyl)benzaldehyde (**2**)*

4′-(4-*trans*-pentylcyclohexyl)benzonitrile, 5.0 g (19.6 mmol), was dissolved in 250 ml dry dichloromethane and the solution was cooled to −78°C. Diisobutylaluminium hydride, 23.5 ml of a 1 M solution in dichloromethane (23 mmol), was added dropwise to the stirring cold nitrile solution over a period of 10 min. The reaction was stirred at −78°C for 1.5 h then warmed to room temperature and stirred for an additional 3 h. Water, 60 ml, was added cautiously to the stirring solution causing formation of copious white precipitate and the mixture was stirred for 5 min. 1 M H_2SO_4, 175 ml, was added and the reaction was stirred at room temperature for 1 h. The organic layer was separated and washed with two equal portions of water, one portion of saturated sodium bicarbonate, and one portion of brine. The solution was dried over $MgSO_4$ and removed under vacuum to leave 4.6 g of light yellow oil (90%). The product was used without further purification. ^{1}H NMR (300 MHz, CDCl3) δ 0.88 (t, J = 6.4 Hz, 3H), 1.06 (m, 2H), 1.27 (m, 9H), 1.47 (m, 2H), 1.87 (d, J = 10.6 Hz, 4H), 2.53 (tt, J = 12.6, 3.5 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.77 (d, J = 9.2 Hz, 2H), 9.95 (s, 1H); ^{13}C NMR (75 MHz, CDCl3) δ 14.10, 22.70, 26.61, 32.19, 33.40, 34.00, 37.25, 37.29, 45.01, 127.55, 129.94, 134.59, 155.26, 192.00.

2.2.3 *4′-(4-trans-pentylcyclohexyl)styrene (**3**)*

Methyltriphenylphosphonium bromide, 4.97 g (11.6 mmol), was suspended in dry THF and cooled to 0°C. Butyllithium, 8 ml of a 1.6 M solution in hexanes (12.8 mmol), was added in two 4 ml portions over a period of 3 min causing immediate formation of a deep orange colour. The suspension was stirred at 0°C for 10 min, then warmed to room temperature and stirred an additional 10 min. 4′-(trans-4-pentylcyclohexyl)-benzaldehyde, 3 g (11.6 mmol), was dissolved in 100 ml dry THF. The orange ylide solution was transferred via cannula to the aldehyde solution at room temperature causing immediate disappearance of the orange colour. The reaction was brought to reflux and stirred for 1 h, then cooled to room temperature and stirred another 10 h. The THF was removed under vacuum. The remaining solids were triturated with 300 ml dry hexanes causing formation of a white gummy solid. The hexane slurry was poured through a slug of silica gel. The hexanes were removed under vacuum to leave 2.78 g of a turbid liquid crystal (93%). ^{1}H NMR (400 MHz, CDCl3) δ 0.92 (t, J = 7.04 Hz, 3H), 1.08 (m, 2H), 1.31 (m, 11H), 1.88 (m, 4H), 2.47 (tt, J = 3.27, 12.1 Hz, 1H), 5.19 (d, J = 10.8 Hz, 1H), 5.71 (d, J = 17.6 Hz, 1H), 6.7 (dd, J = 10.8, 17.6 Hz, 1H), 7.18 (d, J = 8.21 Hz, 2H), 7.34 (d, J = 8.21 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 14.1, 22.7, 26.7, 32.2, 33.6, 34.3, 37.3, 37.4, 44.4, 112.8, 126.1, 127.0, 135.3, 136.8, 147.7. Analysis calculated for $C_{19}H_{29}$: C, 88.99; H, 11.01; found: C, 88.51; H, 10.86.

2.2.4 *(S)-1-[4′-(4-trans-pentylcyclohexyl)phenyl]-ethane-1,2-diol (**4**)*

AD-mix-α (Sigma-Aldrich), 10.9 g (1.4 g/mmol alkene), was added to 75 ml water at room temperature with stirring. *Tert*-butanol, 75 ml, was added and the mixture stirred at room temperature for 10 min at which time everything was dissolved. Methyl sulphonamide, 0.74 g (7.81 mmol), was added with stirring and the solution was cooled to 0°C. 4′-(4-*trans*-pentylcyclohexyl)styrene, 2.0 g (7.81 mmol), dissolved in 20 ml *tert*-butanol, was added to the cold solution causing immediate turbidity. Another 25 ml *tert*-butanol was added but the yellow turbidity persisted. The heterogeneous mixture was stirred at 0°C for 48 h.

Sodium sulphite, 10 g (79.3 mmol), was added at 0°C and the stirring mixture was warmed to room temperature over 1 h. Water, 100 ml, and ether, 150 ml, were added. The layers were separated and the aqueous layer was extracted with another 50 ml of ether. The ether layers were combined and washed with two equal portions of water, two equal portions of 1 M HCl, and one equal portion of saturated aqueous sodium chloride. The ethereal solution was dried over $MgSO_4$ and removed under vacuum to leave a yellow slurry. The slurry was put under high vacuum and heated to remove remaining *tert*-butanol. The crude product was recrystallised from dichloromethane/hexanes to give 2.1 g of colourless plates (90%). m.p. 108–110°C; ^{1}H NMR (300 MHz, CDCl3) δ 0.88 (t, J = 7.04 Hz, 3H), 1.04 (m, 2H), 1.27 (m, 99H), 1.43 (m, 2H), 1.84 (d, J = 10.55 Hz, 4H), 2.22 (dd, J = 7.33, 4.99 Hz, 1H), 2.43 (tt, J = 12.02, 2.93 Hz, 1H), 2.61 (d, J = 3.41 Hz, 1H), 3.69 (m, 2H), 4.75 (m, 1H), 7.18 (d, J = 4.10 Hz, 2H), 7.26 (d, J = 4.10 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 14.09, 22.70, 26.63, 32.19, 33.57, 34.31, 37.29, 37.36, 44.33,

68.01, 74.58, 126.05, 127.02, 137.88, 147.84; MS *m/e* calculated for $C_{19}H_{31}O_2Na$ ($M+Na^+$): 313.2138; found 313.2135.

2.2.5 *4′-(4-trans-pentylcyclohexyl)benzoyl chloride (**5**)*

To a flame-dried flask equipped with a reflux condenser and drying tube was added 4′-(4-pentyl-cyclohexyl)benzoic acid, 0.13 g (0.47 mmol), and 25 ml thionyl chloride. The suspension was brought to reflux at which time all of the acid dissolved. The reaction was stirred at reflux for 1 h. The reflux condenser was replaced with a short-path still head and the thionyl chloride was removed at atmospheric pressure over a period of 20 min to leave a dark amber liquid. The flask was placed under aspirator vacuum with an in-line drying tube and heated to remove traces of thionyl chloride. The product was used without further purification. ^{1}H NMR (300 MHz, CDCl3) δ 0.88 (t, J = 6.2 Hz, 3H), 1.02 (m, 2H), 1.25 (m, 9H), 1.44 (m, 2H), 1.87 (m, 4H), 2.58 (tt, J = 12.6, 3.5 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 14.1, 22.7, 26.6, 32.2, 33.3, 33.9, 37.2, 37.3, 44.9, 127.5, 130.9, 131.7, 156.4, 168.0.

2.2.6 *RD2*

(S)-1-[4-(4-pentyl-cyclohexyl)phenyl-ethane-1,2-diol, 0.067 g (0.23 mmol), was dissolved in 10 ml dry dichloromethane. Triethylamine, 0.20 ml (1.41 mmol), and 4-dimethylamino pyridine, 0.057 g (0.47 mmol), were added to the diol solution at room temperature. The crude 4-pentyl-4′-cyclohexylbenzoyl chloride, dissolved in 5 ml dry dichloromethane, was added at room temperature and the reaction was stirred for 24 h. The reaction was diluted with 50 ml dichloromethane and washed with three equal portions of 1 M HCl, one equal portion of saturated sodium bicarbonate, and one equal portion of saturated sodium chloride. The organic layer was dried over magnesium sulphate and removed under vacuum to leave an amber wax. The crude product was chromatographed through silica gel with 96:4/hexanes: ethyl acetate to give 0.138 g of a colourless glass (75%). ^{1}H NMR (300 MHz, CDCl3) δ 0.88 (t, J = 6.45 Hz, 9H), 1.04 (m, 6H), 1.26 (m, 27H), 1.44 (m, 6H), 1.85 (d, J = 11.1 Hz, 12H), 2.46 (m, 3H), 4.68 (dd, J = 12.0, 8.5 Hz, 1H), 6.34 (dd, J = 8.5, 3.5 Hz, 1H), 7.20 (m, 6H), 7.40 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 14.10, 22.70, 26.61, 32.19, 33.43, 33.57, 34.02, 34.24, 37.25, 37.31, 37.36, 44.37, 44.76, 44.78, 66.69, 73.77, 126.70, 126.89, 126.91, 127.15, 127.42, 127.69, 129.82, 129.88, 134.15, 148.35, 153.48, 153.54, 165.71, 16.32. Analysis calculated for $C_{55}H_{78}O_4$: C, 82.24; H, 9.79; found: C, 82.07; H, 9.60.

2.3 *Preparation of Mosher esters*

2.3.1 *(2-hydroxy-2-phenyl)-ethyl 3,3,3-trifluoro-2-(R)-methoxy-2-phenylpropanoate*

To a flame-dried flask was added N,N'-dicyclohexylcarbodiimide, 0.122 g (0.54 mmol), 4-(dimethylamino)pyridine, 0.0025 g (0.02 mmol), 1-hydroxybenzotriazole, 0.036 g (0.54 mmol), and 3.5 ml dry dichloromethane. 1-phenyl-1,2-ethanediol, 0.054 g (0.39 mmol) was added in one portion at room temperature. (R)-(+)-α -methoxy-α -(trifluoromethyl)phenylacetic acid, 0.10 g (0.43 mmol), was added in one portion causing immediate turbidity. The reaction was stirred at room temperature for 24 h. The reaction mixture was then diluted with 40 ml ether and washed with 2 × 30 ml 1M HCl, 2 × 30 ml saturated aqueous sodium bicarbonate and 1 × 30 ml of brine. The ethereal layer was dried over anhydrous magnesium sulphate, filtered through a fine sintered glass funnel, and the solvent was removed under vacuum. The glassy crude product was redissolved in hexanes and filtered again to remove dicyclohexylurea. The hexanes were removed under vacuum to leave 103 mg of a glassy solid. 400 MHz NMR analysis was performed on the crude product.

2.3.2 *Mosher esters of 1-phenyl-1,2-ethane diol*

The same procedure was used to synthesise the Mosher esters of 1-phenyl-1,2-ethane diol enriched in the (S) enantiomer, the product of Sharpless asymmetric dihydroxylation of styrene, and chiral diol **4**.

2.4 *Determination of helical twisting power*

RD2 was dissolved in various nematic hosts and droplets of the N* mixtures were then suspended in glycerol. The LC/glycerol suspensions were examined under an Olympus BX51 polarising microscope equipped with an Instec temperature-controlled hot stage. Droplet images were imported into Adobe Photoshop® and the spacing of extinction lines was measured against a calibrated stage micrometer. A minimum of three droplets were examined at three different concentrations of **RD2** from about 0.3 to 2.0 wt% in each host. HTP was determined from the slope of a plot of 1/pitch versus concentration. Linearity of the data forced to include the origin was confirmed by linear regression ($R \geq 0.9989$).

3. Results and discussion

Our starting material was the commercially available nematogen **1** shown in Scheme 1. Reduction to the aldehyde followed by reaction with methylene-triphenylphosphane gave *trans*-4-pentyl-4′-cyclohexylstyrene

3. Mesogens like nitrile **1** with polar terminal functional groups are known to form head-to-head dimers in the LC phase via dipole-dipole interactions [14, 15]. Given the relatively small dipole moment of 4-alkylstyrenes (around 0.5 D), it was somewhat surprising to find that **3** forms a fairly broad nematic phase from 13.8°C to 46.5°C.

Sharpless asymmetric dihydroxylation [16] of styrene **3** affords (S) chiral diol **4**. The enantiopurity and absolute stereoconfiguration of **4** were determined by synthesising the primary Mosher esters of racemic 1-phenyl-1,2-ethanediol, the same racemate enriched in the (S) enantiomer, the asymmetric dihydroxylation product of styrene, and chiral diol **4**. Acylation of 1-phenyl-1,2-ethanediol and **4** occurs almost exclusively on the primary alcohol. However, since an excess of Mosher's acid ((R)-(+)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid) was employed, traces of the diester were also seen. The methoxy resonances of the diasteriomeric (R),(R) and (S),(R) primary Mosher esters of racemic 1-phenyl-1,2-ethanediol are clearly discernable in the 400 MHz ^{1}H NMR at 3.520 ppm and 3.505 ppm, respectively, as shown in Figure 2. We first analysed racemic 1-phenyl-1,2-ethane diol, then spiked the racemate with pure (S) enantiomer. Given that the stereogenic centre on Mosher's acid remained invariant, we could absolutely determine which methoxy resonance corresponded to the (S) and (R) stereoconfiguration of the chiral diol. The fact that we could resolve the methoxy groups of both diasteriomeric esters is noteworthy, as Mosher esters are typically generated directly on the stereogenic carbinol. Examination of 400 MHz ^{1}H NMR spectra showed no detectable amount of the diasteriomeric ester derived from the (R)-diol in either the asymmetric dihydroxylation product of styrene or chiral diol **4**.

Finally, esterification of chiral diol **4** with two equivalents of the acid chloride **5** gives the new chiral nematic twist agent **RD2**. Unlike the crystalline S1011, **RD2** is a glass at room temperature giving rise to exceptional solubility in nematic hosts. While not mesogenic itself, contact preparations indicate that **RD2** is essentially miscible with the nematic host E7 (i.e. soluble at $\geq$50% doping). A 26% mixture in E7 remains fully dissolved indefinitely at room temperature.

The HTP of **RD2** was determined in five different room-temperature nematic hosts at 25°C utilising the so-called 'droplet' method [17, 18]. HTP was obtained from the slope of a plot of dopant concentration versus 1/helical pitch as shown in Figure 3. Two of the five hosts, E7 and ZLI2806, are commercial mixtures and have positive and negative dielectric anisotropy, respectively. The other three are pure compounds:

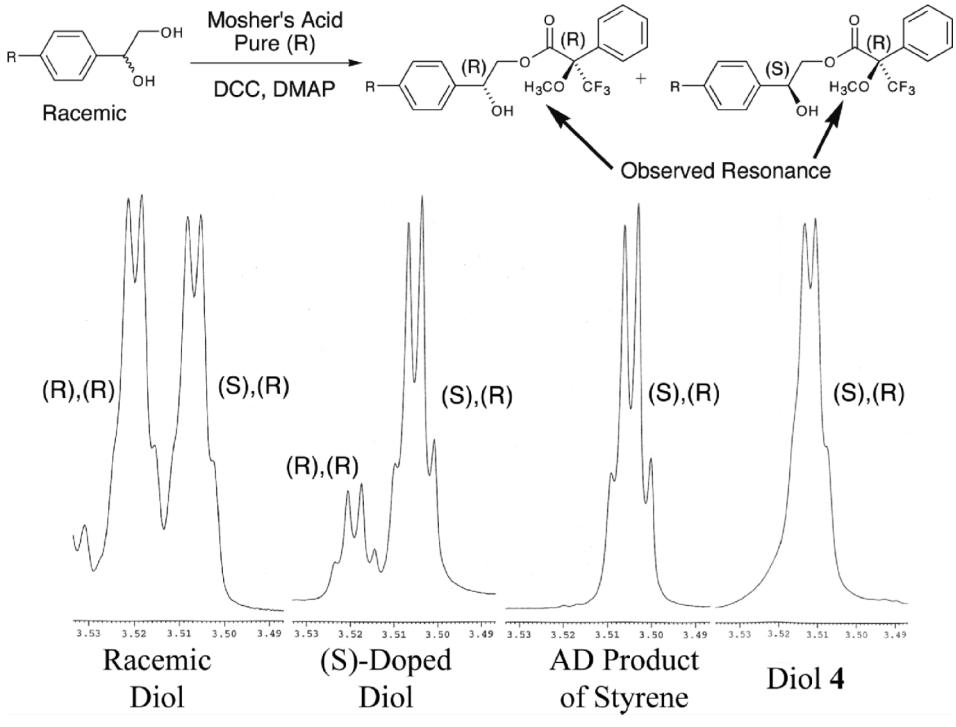


Figure 2. Partial 400 MHz nuclear magnetic resonance spectra of primary Mosher esters of chiral diols (197 × 148 mm^2, 300 × 300 dpi^2).

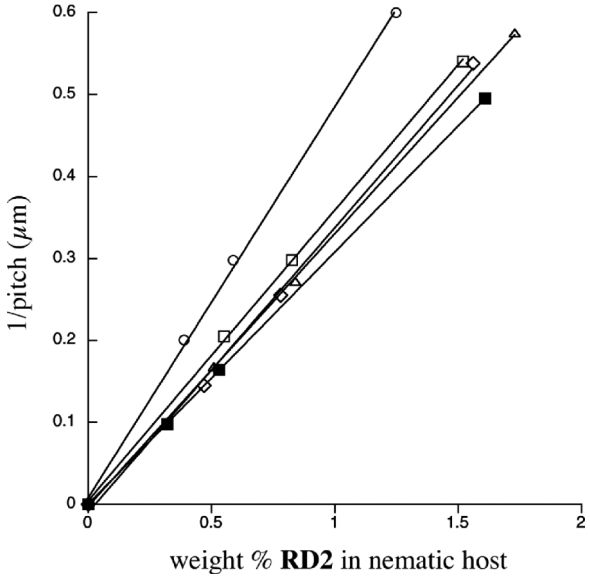


Figure 3. Plot of **RD2** concentration versus inverse of pitch in various nematic hosts: ○ = Cy6ITC; □ = 5CB; ◇ = alkene **3**; ■ = ZLI2806; Δ = E7 (141 × 142 mm^2, 300 × 300 dpi^2).

4′-pentyl-4-biphenylcarbonitrile (5CB), 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6CyITC) and styrene **3** above.

As shown in Table 1, HTP ranges from about +31 to +35 μm^{-1} in four of the hosts, and jumps to almost +48 μm^{-1} in the isothiocyanate 6CyITC. The origins of this roughly 45% increase in HTP is yet unknown. While these HTP values are similar to S1011 by weight, they represent a 7.9% increase in HTP for **RD2** compared with S1011 in E7 on a molar basis.

Table 1. Helical twisting power of **RD2** in nematic hosts at 25°C.

Nematic host	HTP (μm^{-1})
E7	+33.2
ZLI2806	+30.7
5CB	+35.4
Styrene **3**	+35.2
6CyITC	+47.7

(Since nematic hosts are often proprietary mixtures of several different compounds, calculating the molarity of dopant solutions is often not possible. Thus, we calculate dopant concentration based upon weight per cent.) Like S1011, HTP of **RD2** is invariant with temperature in E7 from 25°C to the clearing point of 57°C as shown in Figure 4.

The sign of β was determined by making contact preparations with **RD2**/host and S1011/E7, wherein the two different N* mixtures were allowed to flow together under a polarising microscope. S1011 induces a right-handed helix (+β) in E7. Thus, when mixed with an N* material of opposite helical sense (-β), a region of compensated nematic phase (i.e. N* with infinite pitch) appears at the boundary between the two N* phases. None of the five **RD2** mixtures showed formation of a compensated nematic phase when mixed with S1011/E7 indicating all five mixtures have the same helical sense as S1011/E7.

Finally, not only is **RD2** extremely efficient at inducing N* phases, but a 26% mixture in E7 (pitch around 0.12 μm) also exhibits a blue phase from 21.6°C to

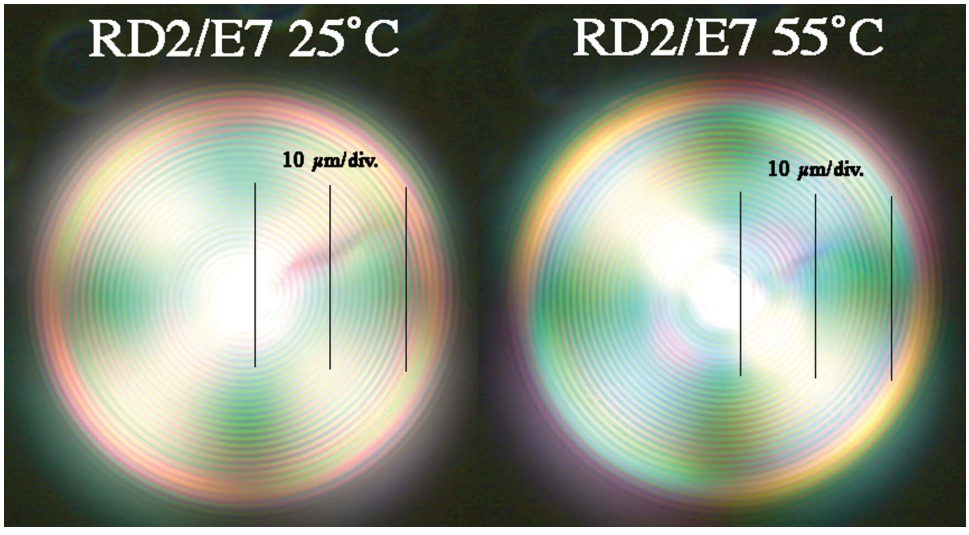


Figure 4. Polarised optical micrographs of N* droplets of **RD2**/E7 in glycerol (303 × 165 mm^2, 72 × 72 dpi^2).

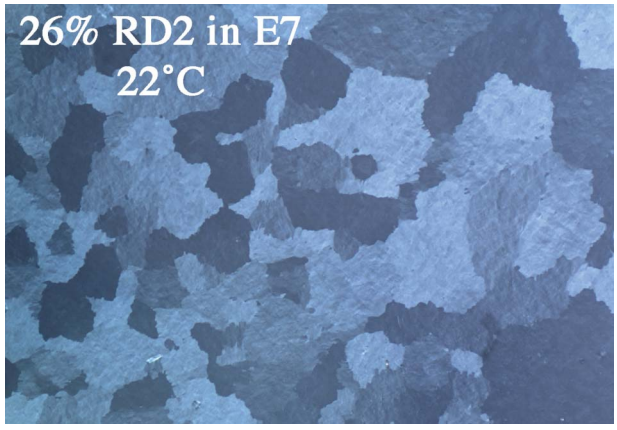


Figure 5. Polarised optical micrograph of 26% **RD2** in E7 (122×84 mm^2, 300×300 dpi^2).

22.8°C. A mosaic texture is observed by polarised optical microscopy as shown in Figure 5, resulting in our tentative assignment of BPIII. Careful calorimetric study of mixtures of different dopant concentrations may reveal additional blue phases. Thus, we believe **RD2** is a valuable new twist agent for the induction of short-pitch chiral nematics and blue phases requiring a single chiral dopant. Moreover, the synthetic strategy outlined above will allow us to introduce polymerisable moieties into **RD2** in order to create polymer-stabilised, room-temperature blue phases.

4. Conclusions

A highly soluble and effective chiral nematic twist agent was synthesised from a commercially available alkylcyclohexyl-benzonitrile nematogen via the Sharpless asymmetric dihydroxylation. The new twist agent **RD2** is suitable for creating tight-pitch N* and blue phase materials requiring a single chiral dopant.

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