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Cholesterol based photo-switchable mesogenic dimers. Strongly bent molecules versus intercalated structure.

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1. Materials and Instruments

All substrates were purchased from Sigma Aldrich and used without further purification. The solvents used: trichloromethane, dichloromethane, dimethylformamide, acetone, toluene, tetrahydrofuran, ethanol and methanol were of p. a. quality. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 (Merck) pre-coated aluminum plates (0.25 mm thickness) and visualized using UV lamp (254 nm). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

Optical rotations were measured in chloroform using a Perkin-Elmer model 343 polarimeter at 22°C. Ultraviolet (UV) absorption spectra were obtained on a Shimadzu UV- 2401PC UV spectrophotometer in chloroform.

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent 400 MHz NMR spectrometer. Proton chemical shifts were reported in ppm (δ) relative to the internal standard – tetramethylsilane (TMS, δ = 0.00 ppm). Carbon chemical shifts are reported in ppm (δ) relative to the residual solvent signal ($CDCl_3$, δ = 77.0 ppm). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constant (Hz). In all recorded spectra, there were also sharp signals originating from small amount of known impurities present in the used solvents: H_2O (1.7 ppm), $CHCl_3$ (7.27 ppm).

The differential scanning calorimetry measurements were performed on a NETZSCH DSC 204 Phoenix system, 1-2 mg samples were prepared and investigated. Experiments were carried out in a sealed aluminum crucible at a cooling-heating rate of 10°C/min using N_2 as a protective gas. For analyzing of the phase transitions temperatures and enthalpies, NETZSCH Proteus – Thermal Analysis – Version 6.0.0 software was applied.

For the optical studies, Olympus SZX16 polarizing microscope equipped with temperature Controlled Microscope Stage – Linkam LTS420 with Linkam T95-HS Heating/Cooling Stage System Controller and Linksys32 version 2.2.9 software was used. For optical studies, glass cells, having ITO electrodes and polymer aligning layer, were used of various thickness (1.5 to 10 microns).

The X-ray diffraction data for all crystals were collected using Bruker D8 Venture diffractometer with CMOS-type Photon100 area detector and GN2-flow LT device. Single crystal diffraction data for **C-2**, **C-3**, **C-4** and **C-7** compounds were collected at 100K and for **C-6** and **C-8** at 125K using TRIUMPH monochromated CuKα radiation (λ = 1.54178 Å). The data treatment and reduction were done using the

Bruker suite of programs [1]. The structures were solved by direct methods and refined using the SHELXL program suite [2,3,4,5]. The atomic scattering factors were taken from the International Tables for Crystallography [6]. For the preparations of crystal structure figures, the Mercury CSD 3.9 software was used [7]. The crystal structures were deposited with the Cambridge Crystallographic Data Centre under the following deposition numbers: 1871483 - 1871488.

The small angle X-ray diffraction (SAXRD) patterns for the powder as well as partially aligned samples were obtained on a low-angle Nanostar-U Bruker diffractometer working in transmission geometry with Cu lamp emitting radiation with a length of 1.54056 Å, powered by 50 kV voltage, and of 600 μA current. The device was equipped with a crossed Goebel mirrors which allow to obtain a parallel beam having a diameter of 500 μm. X-ray patterns were registered with an area detector VANTEC2000. The temperature of the sample was controlled with precision of 0.1K. Samples were prepared in thin-walled glass capillaries.

Wide angle X-ray Powder Diffraction data were collected on a Bruker D8 Discover diffractometer equipped with capillary stage, sealed tube with Cu anode, Goebel focusing mirror and LynxEye detector. The 2θ range for the data collection was 3°-30°. Further processing of the data was performed by the DIFFRAC EVA [8].

For the sample irradiation with UV light, the fluorescent light source Philips TLD 18w/08 was used.

2. Organic synthesis

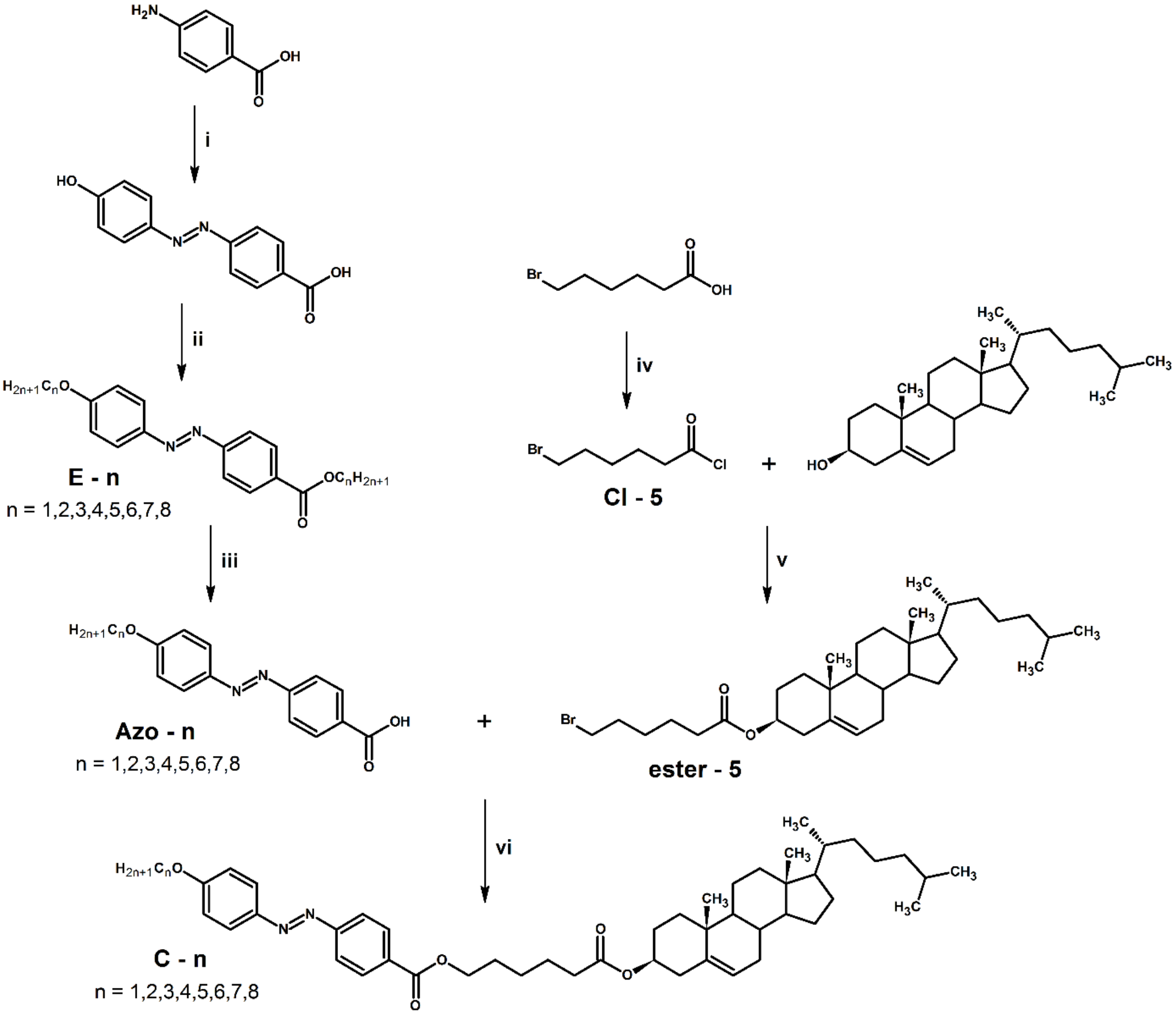
The following abbreviations are used:

DMAP – 4-(dimethylamino)pyridine

DMF – dimethylformamide

THF – tetrahydrofuran

The general procedure for the synthesis of compounds **C-1** – **C-8** is presented in Scheme SI-1.



Scheme SI-1. General procedure for the synthesis of compounds **C-1** – **C-8**. Reagents and conditions: (i) HCl, $NaNO_2$, 5°C; EtOH, NaOH, phenol, 0°C; (ii) $C_nH_{2n+1}Br$, KI, K_2CO_3, DMF, 90°C; (iii) NaOH, EtOH, reflux; (iv) $SOCl_2$, toluene, room temperature; (v) pyridine, DMAP, room temperature; (vi) KI, K_2CO_3, DMF, 90°C.

Preparation of 4-[4’-(hydroxyphenyl)azo]benzoic acid

To a solution of 4-aminobenzoic acid (13.72 g, 0.10 mol; 1 eq) in water (200 mL) and 37% HCl (33.3 mL, 0.40 mol; 4 eq) cooled in an ice bath, a cold solution of $NaNO_2$ (6.90 g, 0.10 mol; 1 eq) in water (180 mL) was added dropwise at such rate that the temperature did not exceed 5°C. Conversion of 4-aminobenzoic acid was monitored by thin-layer chromatography (TLC). The formed solution of diazonium salt was then added to a solution of phenol (9.4 g, 0.10 mol; 1 eq) and NaOH (20.0 g, 0,50 mol; 5 eq) in water (300 mL) at 0°C. The reaction mixture was left for 90 min at room temperature and then acidified with diluted HCl. The formed precipitate was filtered off and recrystallized from hexane to give the product as orange crystals (16.96 g, 70%).

Preparation of 4-[4’-(methoxyphenyl)azo]benzoic acid methyl ester (E-1)

To a solution of 4-[4’-(hydroxyphenyl)azo]benzoic acid (0.97 g, 4.0 mmol; 1 eq) in DMF (50 mL), K_2CO_3 (2.21 g, 16.0 mmol; 4 eq) and KI (1.33 g, 8.0 mmol; 2 eq) were added at room temperature. The mixture was stirred at 50°C for 10 min and a solution of iodomethane (0.56 mL, 9.0 mmol; 2,25 eq) in DMF (10 mL) was added dropwise. The stirring was continued at 90°C for 24 h. Then, the mixture was cooled to the room temperature and poured into distilled water (300 mL) to precipitate the crude product, which was collected by filtration. After washing with methanol, the resulted ester **E-1** (1.02 g, 94%) was dried and its high purity was confirmed by TLC and spectroscopic methods.

Preparation of compounds: **E-2** (92%), **E-3** (90%), **E-4** (94%), **E-5** (92%), **E-6** (92%), **E-7** (90%), and **E-8** (94%), was performed analogously as described above for **E-1** (instead of iodomethane, the corresponding ω-bromoalkane was used).

Preparation of 4-[4’-(methoxyphenyl)azo]benzoic acid (Azo-1)

A solution of NaOH (140 mg, 3.5 mol; 1 eq) in water (5 mL) was added slowly to a stirred suspension of the **ester E-1** (0.945 g, 3.5 mmol; 1 eq) in EtOH (50 mL). The reaction mixture was refluxed for 2 h. Then it was cooled to the room temperature and poured into distilled water (200 mL). The yellow precipitate was filtered and washed with a small volume of methanol. The resulted acid **Azo-1** (0.88 g, 98%) was dried and its purity was confirmed by TLC and spectroscopic methods.

An analogous procedure to this described above was used to obtain compounds: **Azo-2** (96%); **Azo-3** (98%); **Azo-4** (98%); **Azo-5** (96%); **Azo-6** (98%); **Azo-7** (96%), and **Azo-8** (96%).

Preparation of 6-bromohexanoyl chloride (Cl-5)

A mixture of 6-bromohexanoic acid (9.75 g, 0.05 mol; 1 eq) and thionyl chloride (7.4 mL. 0.10 mol; 2 eq) was stirred overnight at room temperature. The crude product was purified by vacuum distillation to afford acid chloride **Cl-5** as colorless oil (9.82 g, 92%; bp 110-120°C / 20 mm Hg).

Preparation of cholesteryl 6’-bromohexanoate (ester-5)

To a solution of cholesterol (7.73 g, 0.02 mol; 1 eq) in anhydrous pyridine (75 mL), DMAP (366 mg, 3 mmol; 0.003 eq) was added. The reaction mixture was vigorously stirred at room temperature while a solution of 6-bromohexanoyl chloride (427 g, 0,02 mol; 1 eq) in anhydrous pyridine (15 mL) was added dropwise. The resulted yellowish mixture was stirred for additional 24 h and then poured into distilled water (300 mL). The precipitate was then filtered and recrystallized from EtOH to give the **ester-5** as colorless crystals (9.47 g, 84%): $[\alpha]_D^{25}$ -27.1 (*c* 1.0, $CHCl_3$).

Preparation of cholesteryl 6’-{4’’-4’’’-(methoxyphenyl)azo]benzoyloxy}hexanoate (C-1)

To a solution of 4-[4’-(methoxyphenyl)azo]benzoic acid **(Azo-1)** (256 mg, 1.0 mmol; 1 eq) in DMF (40 mL) at the room temperature was added K_2CO_3 (552 mg, 4.0 mmol; 4 eq) and KI (664 mg, 4.0 mmol; 4 eq). The reaction mixture was stirred at 50°C for 15 min while a solution of cholesteryl 6’-bromohexanoate (564 mg, 1.0 mmol; 1 eq) in dry THF (10 mL) was added dropwise. The mixture was stirred at 90°C for 24 h and then it was cooled to the room temperature, poured into distilled water (100 mL) and extracted with diethyl ether (200 mL). The organic phase was separated and washed with water (2 × 100 mL). Then it was concentrated to 20 mL on a rotary evaporator and diluted with methanol (150 mL). The precipitated crude product **C-1** was filtered off, washed with methanol and dried (496 mg, 67%). Its purity was confirmed by TLC and spectroscopic methods.

An analogous procedure to this described above was used to obtain compounds: **C-2** (68%); **C-3** (66%); **C-4** (67%); **C-5** (68%); **C-6** (69%); **C-7** (66%); and **C-8** (67%).

Spectral characterization of the final compounds

Due to the complex structure of the molecules, for the description of NMR signals, the numbers of carbon atoms were adopted as indicated below. The same numbering was used in description of all crystal structures of investigated compounds. (see Fig. S5.)

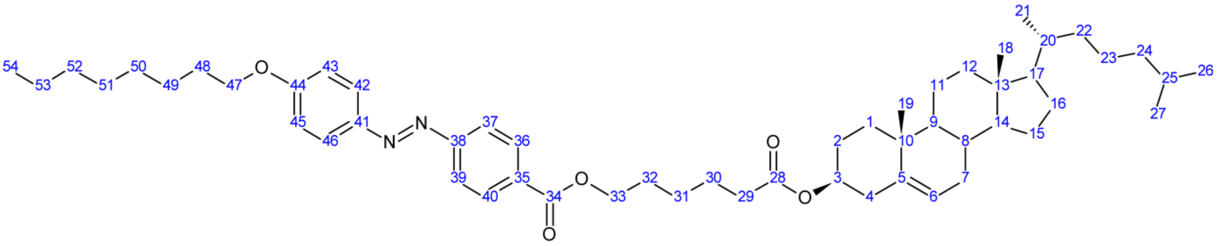


Fig. S1. Carbon atoms numbering adopted for the description of NMR signals.

Cholesteryl 6’-{4’’-[4’’’-(methoxyphenyl)azo]benzoyloxy}hexanoate (C-1)

$[\alpha]_D^{25}$ -14.0 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.63 (3H, s, 18-H_3), 0.86 and 0.87 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H_3), 0.89 (3H, d, *J* = 6.7 Hz, 21-H_3), 0.97 (3H, s, 19-H_3), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H_2), 3.90 (3H, s, 47-H_3), 4.36 (2H, t, *J* = 6.4 Hz, 33-H_2), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 6.99 (2H, m, 43- and 45-H), 7.91 (4H, br m, 37-, 39-, 42- and 46- H), 8.15 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 11.9 (C-18), 18.7 (C-21), 19.3 (C-19), 21.0 (CH_2), 22.6 and 22.8 (C-26 and C-27), 23.9 (CH_2), 24.2 (CH_2), 24.7 (CH_2), 25.6 (CH_2), 27.8 (CH_2), 28.0 (C-25), 28.2 (CH_2), 28.4 (CH_2), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH_2), 36.5 (C-10), 37.0 (CH_2), 38.1 (CH_2), 39.5 (CH_2), 39.7 (CH_2), 42.3 (C-13), 50.0 (C-9), 55.6 (C-47), 56.1 (C-17), 56.6 (C-14), 65.0 (C-33), 73.8 (C-3), 114.3 (C-43 and C-45), 122.4 (C-42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.4 (C-44), 139.5 (C-5), 147.0 (C-41), 155.3 (C-38), 162.6 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(ethoxyphenyl)azo]benzoyloxy}hexanoate (C-2)

$[\alpha]_D^{25}$ -13.0 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.63 (3H, s, 18-H_3), 0.86 and 0.87 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H_3), 0.89 (3H, d, *J* = 6.7 Hz, 21-H_3), 0.97 (3H, s, 19-H_3), 1.45 (3H, t, *J* = 7.0 Hz, 48-H_3), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H_2), 4.10 (2H, q, *J* = 7.0 Hz, 47-H_2), 4.35 (2H, t, *J* = 6.4 Hz, 33-H_2), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 6.99 (2H, m, 43- and 45-H), 7.91 (4H, br m, 37-, 39-, 42- and 46-H), 8.15 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 11.9 (C-18), 14.7 (C-48), 18.7 (C-21), 19.3 (C-19), 21.0 (CH_2), 22.6 and 22.8 (C-26 and C- 27), 23.9 (CH_2), 24.2 (CH_2), 24.7 (CH_2), 25.6 (CH_2), 27.8 (CH_2), 28.0 (C-25), 28.2 (CH_2), 28.4 (CH_2), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH_2), 36.5 (C-10), 37.0 (CH_2), 38.1 (CH_2), 39.5 (CH_2), 39.7 (CH_2), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C-14), 63.8 (C-47), 64.9 (C-33), 73.8 (C- 3), 114.7 (C-43 and C-45), 122.3 (C-42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C- 36 and C-40), 131.3 (C-44), 139.5 (C-5), 146.8 (C-41), 155.3 (C-38), 162.1 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(propoxyphenyl)azo]benzoyloxy}hexanoate (C-3)

$[\alpha]_D^{25}$ -13.9 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.63 (3H, s, 18-H_3), 0.85 and 0.86 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H_3), 0.90 (3H, d, *J* = 6.7 Hz, 21-H_3), 0.97 (3H, s, 19-H_3), 1.06 (3H, t, *J* = 7.4 Hz, 49-H_3), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H_2), 4.00 (2H, t, *J* = 6.6 Hz, 47-H_2), 4.35 (2H, t, *J* = 6.4 Hz, 33-H_2), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 7.00 (2H, m, 43- and 45-H), 7.91 (4H, br m, 37-, 39-, 42- and 46-H), 8.15 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, $CDCl_3$) δ 10.5 (C-49), 11.9 (C-18), 18.7 (C-21), 19.3 (C-19), 21.0 (CH_2), 22.5 (C-48), 22.6 and 22.8 (C- 26 and C-27), 23.9 (CH_2), 24.2 (CH_2), 24.7 (CH_2), 25.6 (CH_2), 27.8 (CH_2), 28.0 (C-25), 28.2 (CH_2), 28.4 (CH_2), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH_2), 36.5 (C-10), 37.0 (CH_2), 38.1 (CH_2), 39.5 (CH_2), 39.7 (CH_2), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C-14), 64.9 (C-33), 69.8 (C-47), 73.8 (C-3), 114.7 (C-43 and C-45), 122.3 (C-42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.3 (C-44), 139.5 (C-5), 146.8 (C-41), 155.3 (C-38), 162.1 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(butoxyphenyl)azo]benzoyloxy}hexanoate (C-4)

$[\alpha]_D^{25}$ -11.2 (*c* 1.0, CHCl$_3$); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 0.64 (3H, s, 18-H$_3$), 0.85 and 0.86 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H$_3$), 0.90 (3H, d, *J* = 6.7 Hz, 21-H$_3$), 0.97 (3H, s, 19-H$_3$), 1.00 (3H, t, *J* = 7.4 Hz, 50-H$_3$), 2.28 (2H, m), 2.33 (2H, t, *J* = 7.3 Hz, 29-H$_2$), 4.05 (2H, t, *J* = 6.6 Hz, 47-H$_2$), 4.36 (2H, t, *J* = 6.4 Hz, 33-H$_2$), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 7.00 (2H, m, 43- and 45-H), 7.91 (4H, br m, 37-, 39-, 42- and 46-H), 8.15 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, CDCl$_3$) δ 11.9 (C-18), 13.6 (C-50), 18.7 (C-21), 19.2 (CH$_2$), 19.3 (C-19), 21.0 (CH$_2$), 22.6 and 22.8 (C- 26 and C-27), 23.9 (CH$_2$), 24.2 (CH$_2$), 24.7 (CH$_2$), 25.6 (CH$_2$), 27.8 (CH$_2$), 28.0 (C-25), 28.2 (CH$_2$), 28.4 (CH$_2$), 31.2 (CH$_2$), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH$_2$), 36.5 (C-10), 36.9 (CH$_2$), 38.1 (CH$_2$), 39.5 (CH$_2$), 39.7 (CH$_2$), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C-14), 64.9 (C-33), 68.1 (C-47), 73.8 (C-3), 114.7 (C-43 and C-45), 122.3 (C-42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.3 (C-44), 139.5 (C-5), 146.8 (C-41), 155.3 (C-38), 162.3 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(pentyloxyphenyl)azo]benzoyloxy}hexanoate (C-5)

$[\alpha]_D^{25}$ -14.0 (*c* 1.0, CHCl$_3$); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 0.64 (3H, s, 18-H$_3$), 0.85 and 0.86 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H$_3$), 0.90 (3H, d, *J* = 6.7 Hz, 21-H$_3$), 0.95 (3H, t, *J* = 7.2 Hz, 51-H$_3$), 0.97 (3H, s, 19-H$_3$), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H$_2$), 4.04 (2H, t, *J* = 6.6 Hz, 47-H$_2$), 4.36 (2H, t, *J* = 6.4 Hz, 33-H$_2$), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 7.00 (2H, m, 43-H and 45-H), 7.91 (4H, br m, 37-, 39-, 42- and 46-H), 8.16 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, CDCl$_3$) δ 11.9 (C-18), 14.0 (C-51), 18.7 (C-21), 19.3 (C-19), 21.0 (CH$_2$), 22.5 (CH$_2$), 22.6 and 22.8 (C- 26 and C-27), 23.9 (CH$_2$), 24.2 (CH$_2$), 24.7 (CH$_2$), 25.6 (CH$_2$), 27.8 (CH$_2$), 28.0 (C-25), 28.1 (CH$_2$), 28.2 (CH$_2$), 28.4 (CH$_2$), 28.9 (CH$_2$), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH$_2$), 36.5 (C-10), 36.9 (CH$_2$), 38.1 (CH$_2$), 39.5 (CH$_2$), 39.7 (CH$_2$), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C- 14), 64.9 (C-33), 68.4 (C-47), 73.8 (C-3), 114.7 (C-43 and C-45), 122.3 (C-42 and C-46), 122.6 (C- 6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.3 (C-44), 139.5 (C-5), 146.8 (C-41), 155.3 (C-38), 162.3 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(hexyloxyphenyl)azo]benzoyloxy}hexanoate (C-6)

$[\alpha]_D^{25}$ -13.1 (*c* 1.0, CHCl$_3$); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 0.64 (3H, s, 18-H$_3$), 0.86 and 0.87 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H$_3$), 0.89 (3H, d, *J* = 6.7 Hz, 21-H$_3$), 0.91 (3H, t, *J* = 7.2 Hz, 52-H$_3$), 0.98 (3H, s, 19-H$_3$), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H$_2$), 4.05 (2H, t, *J* = 6.6 Hz, 47-H$_2$), 4.36 (2H, t, *J* = 6.4 Hz, 33-H$_2$), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 7.00 (2H, m, 43- and 45-H), 7.92 (4H, br m, 37-, 39-, 42- and 46-H), 8.16 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, CDCl$_3$) δ 11.9 (C-18), 14.0 (C-52), 18.7 (C-21), 19. 3 (C-19), 21.0 (CH$_2$), 22.6 (CH$_2$), 22.6 and

22.8 (C- 26 and C-27), 23.9 (CH$_2$), 24.2 (CH$_2$), 24.7 (CH$_2$), 25.6 (CH$_2$), 25.7 (CH$_2$), 27.8 (CH$_2$), 28.0 (C-25), 28.2 (CH$_2$), 28.4 (CH$_2$), 29.1 (CH$_2$), 31.5 (CH$_2$), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH$_2$), 36.5 (C-10), 36.9 (CH$_2$), 38.1 (CH$_2$), 39.5 (CH$_2$), 39.7 (CH$_2$), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C-14), 64.9 (C-33), 68.4 (C-47), 73.8 (C-3), 114.7 (C-43 and C-45), 122.3 (C- 42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.3 (C-44), 139.6 (C-5), 146.8 (C-41), 155.3 (C-38), 162.3 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(heptyloxyphenyl)azo]benzoyloxy}hexanoate (C-7)

$[\alpha]_D^{25}$ -10.9 (*c* 1.0, CHCl$_3$); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 0.64 (3H, s, 18-H$_3$), 0.86 and 0.87 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H$_3$), 0.88 (3H, t, *J* = 7.2 Hz, 53-H$_3$), 0.89 (3H, d, *J* = 6.7 Hz, 21-H$_3$), 0.98 (3H, s, 19-H$_3$), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H$_2$), 4.04 (2H, t, *J* = 6.6 Hz, 47-H$_2$), 4.36 (2H, t, *J* = 6.4 Hz, 33-H$_2$), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 7.00 (2H, m, 43- and 45-H), 7.92 (4H, br m, 37-, 39-, 42- and 46-H), 8.16 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, CDCl$_3$) δ 11.9 (C-18), 14.0 (C-53), 18.7 (C-21), 19.3 (C-19), 21.0 (CH$_2$), 22.6 (CH$_2$), 22.6 and 22.8 (C- 26 and C-27), 23.9 (CH$_2$), 24.2 (CH$_2$), 24.7 (CH$_2$), 25.6 (CH$_2$), 26.0 (CH$_2$), 27.8 (CH$_2$), 28.0 (C-25), 28.2 (CH$_2$), 28.4 (CH$_2$), 29.1 (CH$_2$), 29.2 (CH$_2$), 31.5 (CH$_2$), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH$_2$), 36.5 (C-10), 36.9 (CH$_2$), 38.1 (CH$_2$), 39.5 (CH$_2$), 39.7 (CH$_2$), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C-14), 64.9 (C-33), 68.4 (C-47), 73.8 (C-3), 114.7 (C-43 and C-45), 122.3 (C-42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.3 (C-44), 139.6 (C-5), 146.8 (C-41), 155.3 (C-38), 162.3 (C-35), 166.1 (C-34), 172.9 (C-28).

Cholesteryl 6’-{4’’-[4’’’-(octyloxyphenyl)azo]benzoyloxy}hexanoate (C-8)

$[\alpha]_D^{25}$ -12.0 (*c* 1.0, CHCl$_3$); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 0.64 (3H, s, 18-H$_3$), 0.86 and 0.87 (3H and 3H, each d, *J* = 6.6 Hz, 26- and 27-H$_3$), 0.88 (3H, t, *J* = 7.2 Hz, 54-H$_3$), 0.89 (3H, d, *J* = 6.7 Hz, 21-H$_3$), 0.98 (3H, s, 19-H$_3$), 2.28 (2H, m), 2.32 (2H, t, *J* = 7.3 Hz, 29-H$_2$), 4.04 (2H, t, *J* = 6.6 Hz, 47-H$_2$), 4.36 (2H, t, *J* = 6.4 Hz, 33-H$_2$), 4.60 (H, br m, 3-H), 5.32 (1H, br d, *J* = 3.9 Hz, 6-H), 7.00 (2H, m, 43- and 45-H), 7.92 (4H, br m, 37-, 39-, 42- and 46-H), 8.16 (2H, m, 36- and 40-H); **^{13}C NMR** (400 MHz, CDCl$_3$) δ 11.9 (C-18), 14.0 (C-54), 18.7 (C-21), 19.3 (C-19), 21.0 (CH$_2$), 22.6 (CH$_2$), 22.6 and 22.8 (C- 26 and C-27), 23.9 (CH$_2$), 24.2 (CH$_2$), 24.7 (CH$_2$), 25.6 (CH$_2$), 26.0 (CH$_2$), 27.8 (CH$_2$), 28.0 (C-25), 28.2 (CH$_2$), 28.4 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 30.7 (CH$_2$), 31.5 (CH$_2$), 31.8 (C-8), 31.9 (C-7), 34.5 (C-29), 35.8 (C-20), 36.2 (CH$_2$), 36.5 (C-10), 36.9 (CH$_2$), 38.1 (CH$_2$), 39.5 (CH$_2$), 39.7 (CH$_2$), 42.3 (C-13), 50.0 (C-9), 56.1 (C-17), 56.6 (C-14), 65.0 (C-33), 68.4 (C-47), 73.8 (C-3), 114.7 (C-43 and C-45), 122.3 (C-42 and C-46), 122.6 (C-6), 125.2 (C-37 and C-39), 130.5 (C-36 and C-40), 131.3 (C-44), 139.6 (C-5), 146.8 (C-41), 155.3 (C-38), 162.3 (C-35), 166.1 (C-34), 172.9 (C-28).

3. Additional experimental results

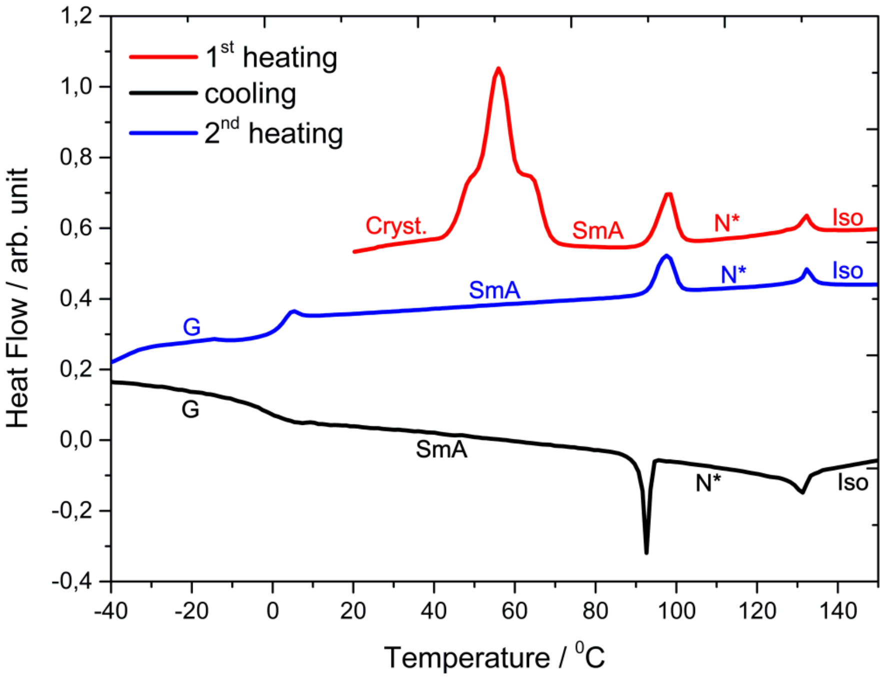


Fig. S2. DSC thermograms (heating and cooling runs) for dimer **C-2**: (red line) first heating run showing SmA - N* phase sequence, (black line) cooling run with N* - SmA phase sequence, on cooling recrystallization does not occur, glassy state is observed at the temperatures below 0°C; (blue line) second heating run, upon heating from glassy state SmA phase is observed at the temperatures above 0°C; G stands for glassy state and Cryst. for crystalline phase.

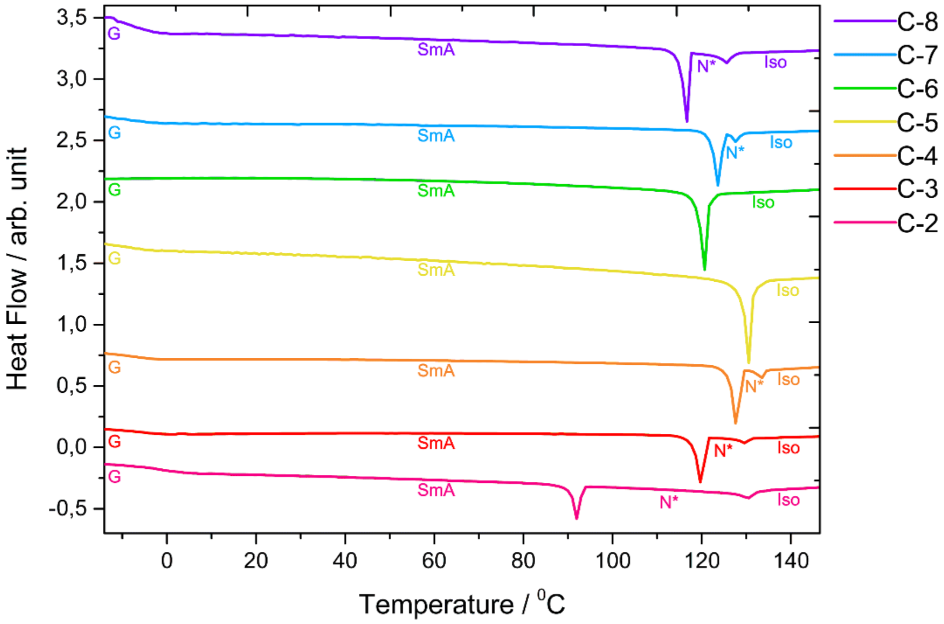


Fig. S3. DSC thermograms (cooling runs) for dimers **C-2** – **C-8** showing N* - SmA phase sequence. G stands for glassy state.

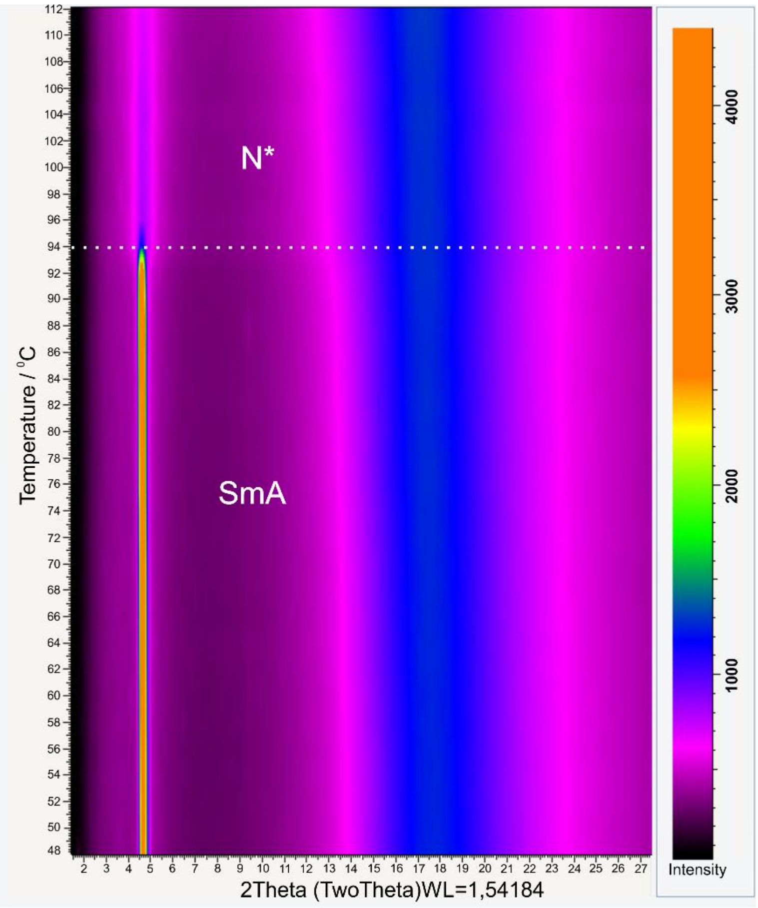


Fig. S4. Temperature evolution of X-ray signal positions for dimer **C-2**. Two distinct regimes corresponding to smectic and chiral nematic phases are clearly visible.

The numbering system

The picture below presents the numbering system on example of the longest compound **C-8**. The numbering of atoms begins with the cholesterol unit (from C1 to C27 atom). This part corresponds to the conventional numbering system for known steroids. The next in the order of numbering is the linker (from O1 through O2 and C28-C34 to O4), then the numbering runs through azobenzene unit (from C35 to C46). The last in the order of numbering is the terminal alkyl chain which, for each chemical compound of the series, differs in the number of carbon atoms.

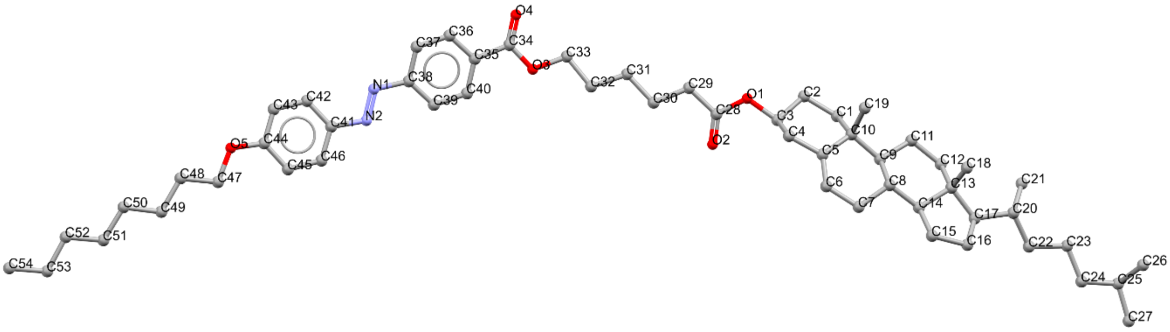


Fig. S5. Numbering system in **C-8** compound

Single crystal X-ray diffraction data processing

C-2

The X-ray measurement of **C-2** was performed at 100(2)K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ = 1.54178 Å). The frames were collected with Bruker APEX2 program [1] and integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33379 reflections to a maximum θ angle of 56.93° (0.92 Å resolution), of which 11292 were independent (average redundancy 2.956, completeness = 98.2%, R_{int}= 5.34%, R_{sig} = 5.15%) and 9171 (81.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.2461(10) Å, b = 10.1265(6) Å, c = 23.6108(14) Å, β = 91.8549(18)°, V = 4360.3(4) Å^3, are based upon the refinement of the XYZ-centroids of 9742 reflections above $20\,\sigma(I)$ with $6.03° < 2\theta < 113.24°$. Data were corrected for absorption effects using the multi-scan method (SADABS) [3].The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.833 and 0.992.

The structure was solved and refined using the Bruker SHELXTL Software Package [4, 5], using the space group $P2_1$, with Z = 4 for the formula unit, $C_{48}H_{68}N_2O_5$. The final anisotropic full-matrix least- squares refinement on F^2 with 1127 variables converged at $R1$ = 5.50%, for the observed data and $wR2$ = 14.57% for all data. The goodness-of-fit was 1.073. The largest peak in the final difference electron density synthesis was 0.306 e$^-$/Å^3 and the largest hole was -0.213 e$^-$/Å^3 with an RMS deviation of 0.048 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.147 g/cm^3 and F(000), 1640 e$^-$. The refined value of absolute structure parameter was -0.05(9) [9].

The non-hydrogen atoms except atoms: C22C, C23C, C24C, C25C, C26C, C27C, C31D, C32D, O4D, O5C, C42C, C43C, C44C, C45C, C46C andC47C were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. In the molecule **(A)** terminal alkyl chain (from atom C20A to C27A) and part of azobenzene unit connected with terminal alkoxy chain (from atom C41A to C48A) were disordered over two positions with an occupancy ratio equal to 0.644:0.356 and 0.580:0.420 respectively. In the molecule **(B)** terminal alkyl chain (from atom C22B to C27B), the linker (from atom C30B to O3B) and (from atom C34B to O4B) were disordered over two positions with an occupancy ratio equal to 0.516:0.484, 0.636:0.364 and 0.708:0.292 respectively. Moreover, pairs of atoms: C20A and C20C, C41A and C41C, C48A and C48C, O3B and O3D, C22B and C22D C30B and C30D, C34B and C34D were constrained to share the same sites. For modeling the reasonable geometry of both molecules during the structure refinement a number of distance and angle restraints were applied.

The atomic scattering factors were taken from the International Tables [6]. Molecular graphics was prepared using program Mercury [7]. Thermal ellipsoids parameters are presented at 50% probability level.

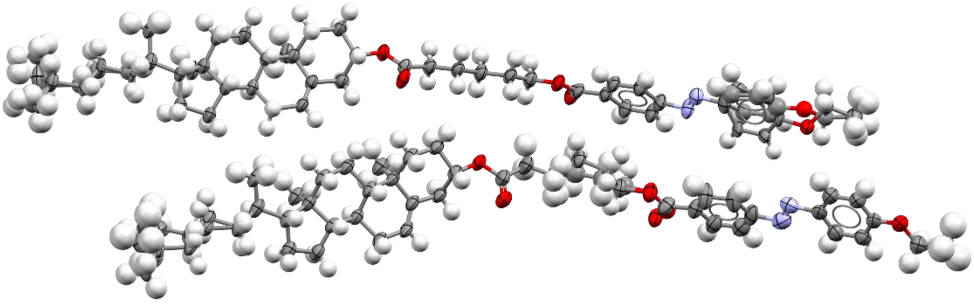


Fig. S6. Molecular structure of cholesteryl 6'-{4''-[4'''-(ethoxyphenyl)azo]benzoyloxy}hexanoate (**C-2**, ellipsoids drawn at 50% probability level)

C-3

The X-ray measurement of **C-3** was performed at 100(2) K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ = 1.54178 Å). The frames were collected with Bruker APEX2 program [1] and integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 28687 reflections to a maximum θ angle of 60.48° (0.89 Å resolution), of which 6483 were independent (average redundancy 4.425, completeness = 98.8%, R_{int} = 4.47%, R_{sig} = 3.59%) and 6277 (96.82%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.1434(6) Å, b = 18.1087(17) Å, c = 39.290(4) Å, V = 4371.0(7) Å^3, are based upon the refinement of the XYZ-centroids of 9871 reflections above 20 $\sigma(I)$ with 5.37° < 2θ < 133.32°. Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.841 and 0.951.

The structure was solved and refined using the Bruker SHELXTL Software Package [4, 5], using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{49}H_{70}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 561 variables converged at R1 = 9.92%, for the observed data and $wR2$ = 21.15% for all data. The goodness-of-fit was 1.120. The largest peak in the final difference electron density synthesis was 0.301 e$^-$/Å^3 and the largest hole was -0.259 e$^-$/Å^3 with an RMS deviation of 0.065 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.166 g/cm^3 and F(000), 1672 e$^-$. The refined value of absolute structure parameter was 0.27(10) [9].

The non-hydrogen atoms except C21B, C27A, C27B, C29B, C30B, C31B, C32B, C33B were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or

1.5 times larger than U_{eq} of the corresponding heavy atom. In the molecule terminal alkyl chain (from atom C23A to C27A) and the linker (from atom C28A to O3A) were disordered over two positions with an occupancy ratio equal to 0.518:0.482 and 0.766:0.234 respectively. Moreover, pairs of atoms: O3A and O3B, C20A and C20B, C23A and C23B, C28A and C28B were constrained to share the same sites. For modeling the geometry of the linker during the structure refinement a number of C-C distance restraints were applied. The atomic scattering factors were taken from the International Tables [6]. Molecular graphics was prepared using program Mercury [7]. Thermal ellipsoids parameters are presented at 50% probability level.

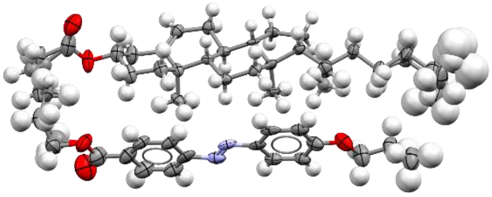


Fig. S7. Molecular structure of cholesteryl 6’-{4’’-[4’’’-(propoxyphenyl)azo]benzoyloxy}hexanoate (**C-3**, ellipsoids drawn at 50% probability level)

C-4

The X-ray measurement of **C-4** was performed at 100(2) K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ = 1.54178 Å). The frames were collected with Bruker APEX2 program [1] and integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 79425 reflections to a maximum θ angle of 67.99° (0.83 Å resolution), of which 16286 were independent (average redundancy 4.877, completeness = 99.9%, R_{int} = 6.74%, R_{sig} = 4.43%) and 13489 (82.83%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.4512(5) Å, b = 10.2622(3) Å, c = 25.1817(7) Å, β = 109.6287(14)°, V = 4491.1(2) Å^3 are based upon the refinement of the XYZ-centroids of 9810 reflections above 20 $\sigma(I)$ with 7.25° < 2θ < 152.67°. Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.835 and 0.991.

The structure was solved and refined using the Bruker SHELXTL Software Package [4, 5], using the space group $P2_1$, with Z = 4 for the formula unit, $C_{50}H_{72}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 1129 variables converged at $R1$ = 5.06%, for the observed data and $wR2$ = 12.91% for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was 0.398 e$^-$/Å^3 and the largest hole was -0.248 e$^-$/Å^3 with an RMS deviation of 0.041 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.155 g/cm^3 and F(000), 1704 e$^-$. The refined value of absolute structure parameter was 0.02(7) [9].

The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. In the molecule **(A)** terminal alkyl chain (from atom C24A to C27A) and terminal alkoxy chain (from atom O5A to C50A) were disordered over two positions with an occupancy ratio equal to 0.823:0.177 and 0.664:0.336 respectively. In the molecule **(B)** terminal alkyl chain (from atom C74A to C77A) and part of azobenzene unit connected with terminal alkoxy chain (from atom N3A to C9TA) were disordered over two positions with an occupancy ratio equal to 0.651:0.349 and 0.800:0.200 respectively. Moreover, pairs of atoms C24A and C24B, O5A and O5B, C74A and C74B, N3A and N3B were constrained to share the same sites. For modeling the reasonable geometry of both molecules during the structure refinement a number of distance and angle restraints were applied. The atomic scattering factors were taken from the International Tables [6]. Molecular graphics was prepared using program Mercury [7]. Thermal ellipsoids parameters are presented at 50% probability level.

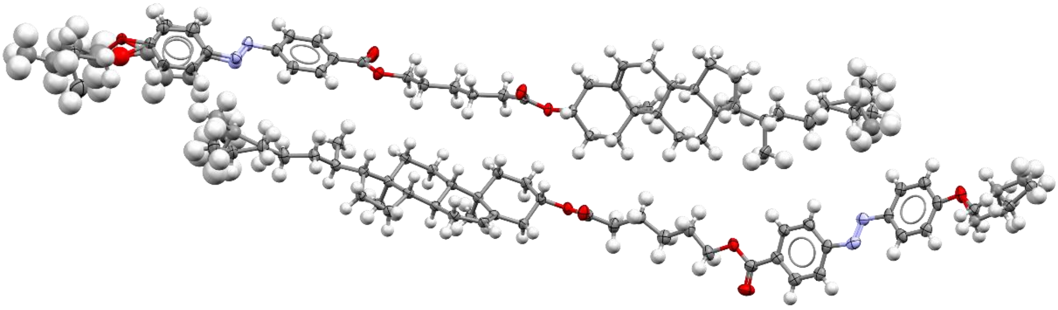


Fig. S8. Molecular structure of cholesteryl 6’-{4’’-[4’’’-(butoxyphenyl)azo]benzoyloxy}hexanoate (**C-4**, ellipsoids drawn at 50% probability level)

<u>C-6</u>

The X-ray measurement of **C-6** was performed at 125(2) K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ = 1.54178 Å). The frames were collected with Bruker APEX2 program [1] and integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 101291 reflections to a maximum θ angle of 66.83° (0.84 Å resolution), of which 16405 were independent (average redundancy 6.174, completeness = 99.6%, R_{int} = 7.10%, R_{sig} = 4.03%) and 14827 (90.38%) were greater than $2\sigma(F^2)$. The final cell constants of a = 19.0707(9) Å, b = 11.2605(5) Å, c = 21.8074(10) Å, β = 96.848(3)°, V = 4649.6(4) Å^3, are based upon the refinement of the XYZ-centroids of 9651 reflections above 20 $\sigma(I)$ with 6.56° < 2θ < 133.38°.

Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8300 and 0.9880.

The structure was solved and refined using the Bruker SHELXTL Software Package [4, 5], using the space group $P2_1$, with $Z = 4$ for the formula unit, $C_{52}H_{76}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 1075 variables converged at $R1 = 4.41\%$, for the observed data and $wR2 = 10.06\%$ for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.393 $e^-/Å^3$ and the largest hole was -0.243 $e^-/Å^3$ with an RMS deviation of 0.038 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.156 g/cm^3 and $F(000)$, 1768 e^-. The refined value of absolute structure parameter was 0.10(8) [9].

The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. For modeling the geometry of the terminal alkyl chain one rigid bond restraint C-C was applied. The atomic scattering factors were taken from the International Tables [6]. Molecular graphics was prepared using program Mercury [7]. Thermal ellipsoids parameters are presented at 50% probability level.

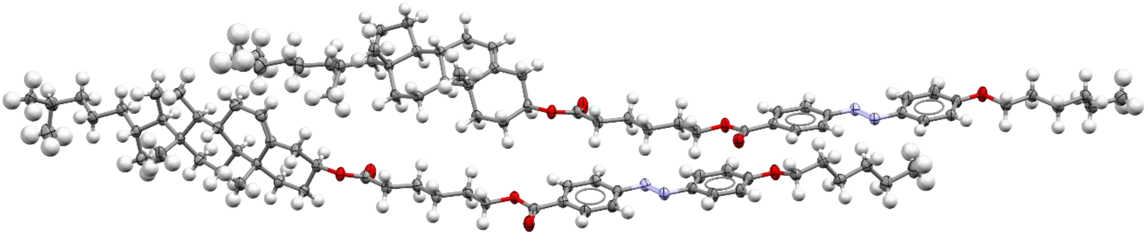


Fig. S9. Molecular structure of cholesteryl 6’-{4’’-[4’’’-(hexyloxyphenyl)azo]benzoyloxy}hexanoate (**C-6**, ellipsoids drawn at 50% probability level)

C-7

The X-ray measurement of **C-7** was performed at 100(2) K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ = 1.54178 Å). The frames were collected with Bruker APEX2 program [1] and integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 27635 reflections to a maximum θ angle of 60.00° (0.89 Å resolution), of which 6953 were independent (average redundancy 3.975, completeness = 99.9%, R_{int} = 3.18%, R_{sig} = 2.64%) and 6406 (92.13%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.4123(6) Å, b = 11.9482(6) Å, c = 16.9850(8) Å, β = 110.830(2)°, V = 2354.3(2) Å^3, are based upon the refinement of the XYZ-centroids of 9857 reflections above 20 $\sigma(I)$ with 5.57° < 2θ < 120.20°.

Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.833 and 0.992.

The structure was solved and refined using the Bruker SHELXTL Software Package [4, 5], using the space group $P2_1$, with $Z = 2$ for the formula unit, $C_{53}H_{78}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 634 variables converged at $R1 = 3.15\%$, for the observed data and $wR2 = 7.16\%$ for all data. The goodness-of-fit was 1.087. The largest peak in the final difference electron density synthesis was 0.143 $e^-/Å^3$ and the largest hole was -0.129 $e^-/Å^3$ with an RMS deviation of 0.038 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.161 g/cm^3 and $F(000)$, 900 e^-. The refined value of absolute structure parameter was 0.00(7) [9].

The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. Azobenzene unit and terminal alkoxy chain (from atom C35 to C53) were disordered over two positions with an occupancy ratio equal to 0.834:0.166. Carbon atoms C47 C47b were constrained to equivalent positions. For modeling the reasonable geometry of both benzene rings during the structure refinement a number of restraints were applied. The atomic scattering factors were taken from the International Tables [6]. Molecular graphics was prepared using program Mercury [7]. Thermal ellipsoids parameters are presented at 50% probability level.

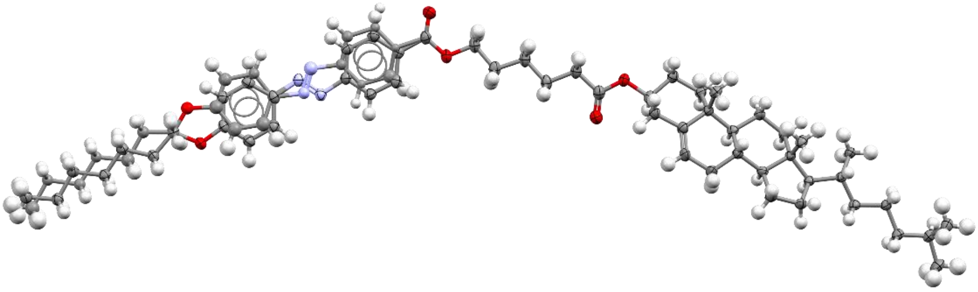


Fig. S10. Molecular structure of cholesteryl 6’-{4’’-[4’’’-(heptyloxyphenyl)azo]benzoyloxy}hexanoate (**C-7**, ellipsoids drawn at 50% probability level)

C-8

The X-ray measurement of **C-8** was performed at 125(2) K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source ($\lambda = 1.54178$ Å). The frames were collected with Bruker APEX2 program [1] and integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 21966 reflections to a maximum θ angle of 65.48° (0.85 Å resolution), of which 7863 were independent (average redundancy 2.794, completeness = 98.0%,

R_{int} = 4.10%, R_{sig} = 4.45%) and 6841 (87.00%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.1746(9) Å, b = 12.1005(9) Å, c = 16.8114(12) Å, β = 103.777(4)°, V = 2405.4(3) Å^3, are based upon the refinement of the XYZ-centroids of 9742 reflections above 20 $\sigma(I)$ with $5.41° < 2\theta < 130.87°$. Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.849 and 0.896.

The structure was solved and refined using the Bruker SHELXTL Software Package [4,5] using the space group $P2_1$, with Z = 2 for the formula unit, $C_{54}H_{80}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 557 variables converged at $R1$ = 4.35%, for the observed data and $wR2$ = 8.92% for all data. The goodness-of-fit was 1.107. The largest peak in the final difference electron density synthesis was 0.229 e$^-$/Å^3 and the largest hole was -0.172 e$^-$/Å^3 with an RMS deviation of 0.042 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.156 g/cm^3 and F(000), 916 e$^-$. The refined value of absolute structure parameter was 0.04(9) [9].

The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables [6]. Molecular graphics was prepared using program Mercury [7]. Thermal ellipsoids parameters are presented at 50% probability level.

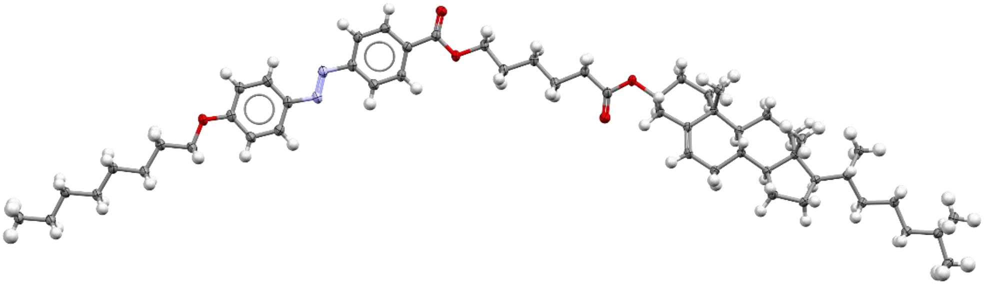


Fig. S11. Molecular structure of cholesteryl 6’-{4’’-[4’’’-(octyloxyphenyl)azo]benzoyloxy}hexanoate (**C-8**, ellipsoids drawn at 50% probability level)

Most of described here crystals are severely disordered with limited scattering power. This results in a few Alerts A and/or B for the following structures: **C-2**, **C-3** and **C-7**.

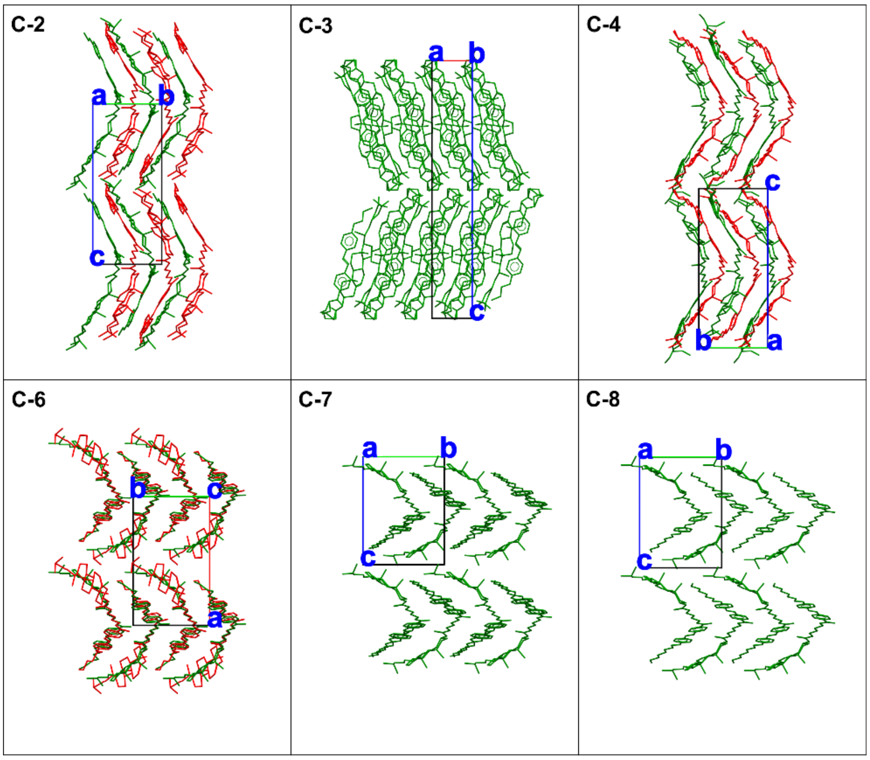


Fig. S12. Crystal packing of **C-2**, **C-3**, **C-4**, **C-6**, **C-7**, and **C-8** compounds (Drawings enlarged from Fig. 8). Hydrogen atoms are omitted for clarity.

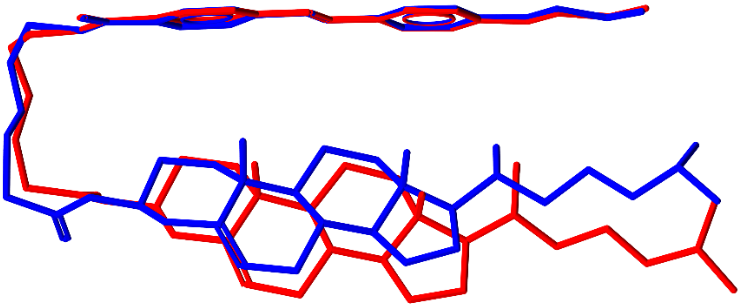


Fig. S13. The difference in molecular shape for dimer **C-3** between the calculated ground state in vacuo (red molecule) and conformation observed in the crystal phase (blue molecule).

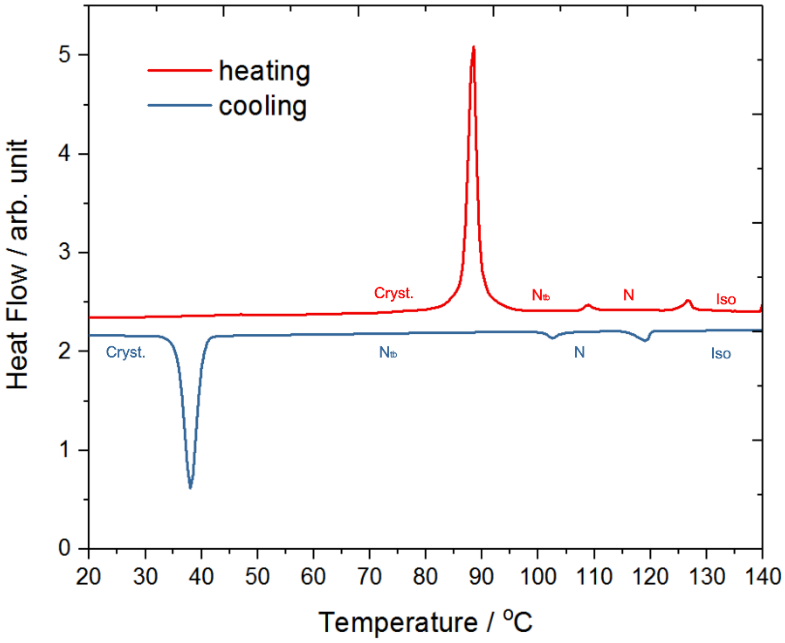


Fig. S14. DSC thermograms (heating and cooling run) for compound **CB9CB**: (red line) heating run showing Cryst. - N_{tb} - N phase sequence, (blue line) cooling run with N - N_{tb} - Cryst. phase sequence; enthalpy change value for transition from crystal phase to N_{tb} phase is 28,51 kJ/mol.

Global parameters: τ, d, φ, LS, LB:

τ - Tilt angle between cholesterol unit and the layer direction. It was determined from the single crystal structures between the appropriate lattice plane and the line passing through the cholesterol unit (from oxygen atom O1 to carbon atom C17).

d - Layer thickness determined from single crystal structures as interplanar distance.

φ - Angle between cholesterol and azo-benzene units. It was determined from single crystal structures between the lines passing through the cholesterol unit (from oxygen atom O1 to carbon atom C17) and azo-benzene unit (from carbon atom C34 to oxygen atom O5). In the case of disorder in the structure, angle was averaged.

LS - Length of the stretched molecules. It was determined from single crystal structures as the sum of length of individual molecule segments. For the molecules of **C-2, C-4, C-6, C-7** and **C-8** it was the sum of the following parts: terminal alkyl chain (from carbon atom C25 to carbon atom C17), cholesterol unit (from carbon atom C17 to oxygen atom O1), linker (from oxygen atom O1 to carbon atom C34), azo-benzene unit (from carbon atom C34 to oxygen atom O5), terminal alkoxy chain (from oxygen atom O5 to carbon atom C48 (in **C-2**), C50 (in **C-4**), C52 (in **C-6**), to C53 (in **C-7**), to C54 (in **C-8**) and methyl group from alkyl linker (as the average length 1.5 Å). Length of **C-3** compound was determined as a sum of: terminal alkyl chain (from carbon atom C25 to carbon atom C17), cholesterol unit (from carbon atom C17 to oxygen atom O1), linker first part (from oxygen atom O1 to carbon atom C29), linker second part (from carbon atom C29 to carbon atom C33), linker third part (from carbon atom C33 to carbon atom C34), azo-benzene unit (from carbon atom C34 to oxygen atom O5), terminal alkoxy chain (from oxygen atom O5 to carbon atom C49) and methyl group from alkyl linker (as the average length 1.5 Å). In the case of disorder in the structure, some distances were averaged.

LB - Length of the completely bent molecule. It was determined from single crystal structures as an average length of two parts of molecule. The first part was determined as a distance from carbon atom C25 to carbon atom C29 plus the average length of methyl group from alkyl linker (1.5 Å). The second part was determined as a distance from the last carbon atom from alkoxy terminal alkyl to carbon atom C32.

Coordinates of optimized unkinked (bent-shaped) C-3 structure:

N	11.89077100	0.72302800	0.70636500
N	12.52017800	0.33069900	-0.31716200
O	-1.81392500	-3.25491500	-0.72870000
O	-0.53015900	-1.47495900	-0.15393800
O	17.66495800	2.20741200	-1.29073300
C	-5.31090600	-2.25041600	-1.70770100
H	-6.00926800	-2.72193800	-2.40828600
H	-5.10452500	-1.24537700	-2.10199500
C	-3.99710400	-3.04701500	-1.70350000
H	-3.56718700	-3.06301300	-2.71231800
H	-4.17155500	-4.09243100	-1.41876200
C	-3.00746600	-2.42438600	-0.72900900
H	-2.71776800	-1.42129900	-1.05623000
C	-3.60096900	-2.35305200	0.68063800
H	-2.89580300	-1.85469000	1.35297200
H	-3.71785600	-3.38601800	1.04098800
C	-4.93213500	-1.62417400	0.69084100
C	-5.13770400	-0.61631100	1.54751900
H	-4.32316200	-0.32014600	2.20936700
C	-6.41608500	0.16005000	1.67968800
H	-6.25906200	1.18087600	1.29167100
H	-6.65666300	0.29144300	2.74394600
C	-7.60015400	-0.49216000	0.94670800
H	-7.95479800	-1.33193900	1.56133800
C	-7.13507500	-1.03044300	-0.43163400
H	-6.68270700	-0.16613700	-0.94591800
C	-5.99264000	-2.09819200	-0.31234000

C	-8.32653300	-1.49243000	-1.30142600
H	-7.97679800	-1.72637800	-2.31424300
H	-8.73828200	-2.42723200	-0.90433200
C	-9.46671000	-0.45935800	-1.40816000
H	-10.26508500	-0.88885300	-2.02271400
H	-9.10445300	0.42917300	-1.94626800
C	-9.98033600	-0.02061400	-0.02151600
C	-8.74282100	0.51346900	0.75329200
H	-8.32960500	1.31498500	0.11651900
C	-9.33760300	1.20742800	1.98669900
H	-8.66596200	1.96285200	2.40757900
H	-9.53399700	0.48084300	2.78518400
C	-10.65928400	1.82629800	1.45567000
H	-10.60474000	2.91936300	1.43811500
H	-11.50163800	1.57148900	2.11047400
C	-10.89337700	1.25509600	0.01503800
H	-10.45321700	1.96407800	-0.70451600
C	-6.53900200	-3.47412000	0.14954100
H	-5.72860400	-4.17749100	0.36318900
H	-7.17134700	-3.93396400	-0.61758100
H	-7.12995400	-3.37664900	1.06624900
C	-10.67275700	-1.19535300	0.70473300
H	-11.50991500	-1.57758500	0.10998800
H	-11.07666700	-0.89597300	1.67754600
H	-9.99404000	-2.03433700	0.88314900
C	-12.39802200	1.13579800	-0.34087200
H	-12.87192400	0.48617900	0.41140100
C	-12.64574300	0.51594400	-1.72676900
H	-12.11554700	1.07546300	-2.50843900
H	-13.71045900	0.52175700	-1.98150800
H	-12.31337900	-0.52406100	-1.77867900
C	-0.64334300	-2.65428000	-0.41464300

C	0.49645700	-3.65731100	-0.42021500
H	0.38712600	-4.30463000	-1.29894300
H	0.35624600	-4.31484900	0.45013000
C	1.87345400	-2.99041600	-0.37775900
H	1.99626200	-2.36239700	-1.27019100
H	1.90312200	-2.30555400	0.47648200
C	3.01862300	-4.01024000	-0.30397700
H	2.91429200	-4.72902300	-1.12825100
H	2.92887800	-4.59822400	0.62160700
C	4.42459200	-3.39250100	-0.38449800
H	5.17147600	-4.19346400	-0.45143400
H	4.51791500	-2.79808900	-1.30291700
C	4.77003500	-2.51359600	0.80970100
H	4.10854300	-1.64713100	0.90106300
H	4.71744800	-3.06992700	1.75260600
O	6.12194200	-2.04272800	0.61849600
C	6.59908700	-1.21425400	1.57564300
O	5.95488200	-0.88702500	2.55415200
C	7.98730200	-0.75375100	1.29040500
C	8.58612200	0.12617400	2.20153800
H	8.02275400	0.43373700	3.07611900
C	9.87610700	0.59089700	1.97523400
H	10.35936500	1.27537400	2.66552300
C	10.58734000	0.18198500	0.83750500
C	9.98862100	-0.70347100	-0.07703500
H	10.55031500	-1.01026800	-0.95186700
C	8.70003500	-1.16444500	0.14981600
H	8.23165100	-1.84462400	-0.55280400
C	13.81461100	0.86503800	-0.46737900
C	14.41732800	1.78124200	0.41057200
H	13.85999000	2.11429900	1.27913200
C	15.70158600	2.25176500	0.16921700

H	16.14835500	2.95890700	0.85847900
C	16.40896100	1.80887600	-0.96411100
C	15.81178100	0.89189600	-1.84533400
H	16.37569400	0.56410000	-2.71261200
C	14.53035300	0.42918300	-1.59623800
H	14.05173200	-0.27865200	-2.26614500
C	18.34529000	3.14176600	-0.44906500
H	18.44271600	2.72717200	0.56474100
H	17.76400300	4.07263000	-0.37982000
C	-13.07782700	2.52426900	-0.24003400
H	-12.67424600	3.17344300	-1.03291400
H	-12.79552900	2.99713900	0.70836000
C	-14.61260000	2.51915700	-0.32215300
H	-14.93765700	2.11823200	-1.28886700
H	-15.01349600	1.83825200	0.44423700
C	-15.21606300	3.91696500	-0.11924300
H	-14.84079200	4.59246600	-0.90389600
H	-14.84454000	4.32520800	0.83225900
C	-16.75695600	3.97559500	-0.10603400
H	-17.11037600	3.26772400	0.66023000
C	-17.37557500	3.56198400	-1.45038900
H	-18.46955200	3.62946900	-1.41559600
H	-17.11852600	2.53358500	-1.72573400
H	-17.02858100	4.22097700	-2.25761200
C	-17.23809700	5.37820600	0.29558600
H	-16.91201700	6.12875000	-0.43659800
H	-16.83946100	5.67320400	1.27366200
H	-18.33233300	5.42342700	0.35080500
C	19.71481600	3.40460500	-1.05962700
H	20.24879700	2.45048400	-1.14504700
H	19.57604600	3.78107200	-2.08030900
C	20.53339400	4.40038900	-0.23193700

H	20.70461900	4.03116500	0.78645500
H	21.51237000	4.57379500	-0.69016800
H	20.02706700	5.37015500	-0.15460400

Coordinates of optimized kinked C-3 structure:

O	-6.11306700	-2.67154500	-0.31965700
O	-6.45652900	-2.84343500	-2.55580800
O	-7.34578800	2.68282100	2.19176000
O	4.88082200	3.86538000	-1.01889800
N	-1.17820000	3.47634900	0.60715800
N	-0.61600000	3.20259400	-0.49160900
C	-2.62195300	-1.29360600	-0.93250600
H	-2.27807300	-0.27453800	-1.14137300
H	-2.33325000	-1.90603100	-1.79846700
C	-4.15490900	-1.28767600	-0.83527100
H	-4.49623300	-0.59439200	-0.05640500
H	-4.58366500	-0.94691200	-1.78400600
C	-4.67123400	-2.68603600	-0.51483200
H	-4.45423600	-3.36160300	-1.34800500
C	-4.05258500	-3.21121500	0.77945000
H	-4.39961700	-4.23212800	0.97348000
H	-4.42815200	-2.58822800	1.60430200
C	-2.53576800	-3.17591900	0.72597400
C	-1.82754300	-4.27216700	1.02416800
H	-2.36391500	-5.18796800	1.27663400
C	-0.32800300	-4.35634000	1.04202100
H	0.00739700	-4.97740700	0.19388200
H	-0.00110300	-4.89777200	1.94080300
C	0.35832500	-2.98190300	0.97512400
H	0.29946400	-2.52634500	1.97390500
C	-0.37824400	-2.07268400	-0.04283800
H	-0.38699100	-2.63939100	-0.98925700

C	-1.88476000	-1.84419000	0.32721200
C	0.39742700	-0.76395800	-0.31467000
H	0.33325800	-0.10160100	0.55570400
H	-0.07616000	-0.21581100	-1.13740600
C	1.88491100	-0.97583500	-0.66252100
H	1.96260200	-1.51340800	-1.61956200
H	2.34506200	0.00506100	-0.81929000
C	2.61794300	-1.79297100	0.42097500
C	1.83133200	-3.12603000	0.56976400
H	1.81979300	-3.56632400	-0.44266000
C	2.75092000	-4.01779900	1.41609100
H	2.54674500	-5.08442700	1.27547200
H	2.61763700	-3.81037300	2.48536300
C	4.17717800	-3.62432000	0.94388600
H	4.65202700	-4.44310600	0.39405200
H	4.82732100	-3.41284200	1.80176700
C	4.03261600	-2.35313500	0.03824400
H	3.95511800	-2.69083100	-1.00763700
C	2.69747000	-1.00145500	1.74562200
H	3.20767800	-0.04379200	1.59382700
H	3.25091700	-1.54705400	2.51727800
H	1.70968500	-0.77572700	2.15679100
C	-2.04453100	-0.84317600	1.50034700
H	-3.08281500	-0.78548400	1.84032400
H	-1.74676000	0.16914700	1.21013200
H	-1.44103200	-1.14547600	2.36273000
C	5.27369700	-1.42619800	0.11590300
H	5.40542900	-1.12783600	1.16777100
C	5.12461300	-0.14757600	-0.72643200
H	6.04048200	0.45230400	-0.70984900
H	4.31827900	0.49539400	-0.36596400
H	4.91030800	-0.39195300	-1.77502100

C	6.54809900	-2.20242400	-0.30098300
H	6.47475600	-2.45545500	-1.37029300
H	6.58095100	-3.15950800	0.23338800
C	7.87748000	-1.47509600	-0.04298100
H	7.91383500	-0.54341500	-0.61919800
H	7.92946500	-1.18380400	1.01748300
C	9.09991400	-2.33850600	-0.38791100
H	9.06796100	-2.60510000	-1.45591600
H	9.02574900	-3.28834200	0.16189800
C	10.46852100	-1.70005700	-0.07495100
H	10.46463300	-1.40866300	0.98729700
C	10.73525700	-0.43704900	-0.90856700
H	11.71800700	-0.01201000	-0.67177900
H	9.98685100	0.34212500	-0.72885300
H	10.72471500	-0.66945100	-1.98189500
C	11.59751000	-2.72235200	-0.27543900
H	11.44649300	-3.61226700	0.34725200
H	12.57378300	-2.29404900	-0.01841200
H	11.64551000	-3.05270300	-1.32149400
C	-6.88855200	-2.75719300	-1.42517200
C	-8.36064200	-2.71727300	-1.05912200
H	-8.55042300	-3.48042500	-0.29522400
H	-8.92158200	-2.98318200	-1.95987200
C	-8.81562200	-1.34276900	-0.52628000
H	-9.87767500	-1.42169700	-0.25578900
H	-8.26981700	-1.12706600	0.39952000
C	-8.62606400	-0.20240000	-1.53743000
H	-9.04158100	-0.50890800	-2.50668400
H	-7.55567500	-0.03252700	-1.70538600
C	-9.29132400	1.12247800	-1.12835000
H	-10.37496100	0.97260100	-1.01945200
H	-9.15844900	1.85770300	-1.93210500

C	-8.79383000	1.73014200	0.17543500
H	-8.92067100	1.05564500	1.02735000
H	-9.32576500	2.65795400	0.41117000
O	-7.38684600	2.02885700	0.02839800
C	-6.77080100	2.50487200	1.13470900
C	-5.32078400	2.76980300	0.91532000
C	-4.56018000	3.18745200	2.01548500
H	-5.05506500	3.31544300	2.97226700
C	-3.19814500	3.42201200	1.87171800
H	-2.58752200	3.73867000	2.71153600
C	-2.57508200	3.23889700	0.62831900
C	-3.34070000	2.84036400	-0.48282200
H	-2.84907200	2.71764900	-1.44107100
C	-4.70107300	2.60688500	-0.33675700
H	-5.29574100	2.29613900	-1.18852600
C	0.77463000	3.42235600	-0.52457300
C	1.53954000	3.91333800	0.54684800
H	1.03754000	4.15766300	1.47643700
C	2.91258200	4.07731800	0.41864700
H	3.48441200	4.45616900	1.25784200
C	3.54804600	3.74933500	-0.79412500
C	2.78724600	3.26351300	-1.87153000
H	3.29730800	3.02013900	-2.79779100
C	1.41797400	3.10411700	-1.73387300
H	0.81423600	2.72886100	-2.55453500
C	5.72894800	4.35228800	0.02508600
H	5.64872500	3.69756500	0.90460300
H	5.40987700	5.36154600	0.32255100
C	7.15490800	4.37070100	-0.50710500
H	7.18469700	4.99865200	-1.40573700
H	7.42323500	3.35517200	-0.82279400
C	8.15256800	4.88532700	0.53529200

H	7.91493800	5.90957000	0.84709600
H	9.16940600	4.89011900	0.12992800
H	8.15642100	4.25547800	1.43308000

4. References

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