Condensation of Free Volume in Structures of Nematic and Hexatic Liquid Crystals

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1.1. General Techniques

Miscellaneous solvents were purchased from Fisher Scientific dried by sequential percolation through columns of activated alumina and copper Q5 catalyst prior to use. Chemical intermediates were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using UV light at wavelengths of both 254 nm and 365 nm. Column chromatography was performed using flash grade silica from Fluorochem (40 - 63μm particle size). Yields refer to chromatographically (HPLC) and spectroscopically (1H NMR and 13C-{1H} NMR) homogenous material.

1.2. Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (1H) and 100.5 MHz (13C-{1H}) as solutions in deuterated chloroform.

1.3. Mass Spectrometry (MS)

Mass spectra were recorded on a Bruker micrOTOF MS-Agilent series 1200LC spectrometer. We thank Mr. Karl Heaton of the University of York for acquiring MS data.

1.4. High Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A quaternary solvent pump, a DGU-20A5 degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector operating at 220/250 nm. The column used was an Alltech C18 bonded reverse-phase silica column with a 5 μm pore size,
an internal diameter of 10 mm and a length of 250 mm. In all cases the mobile phase used was neat acetonitrile, purchased from Fisher Scientific UK.

1.5. Polarised Optical Microscopy (POM)

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured via an InfinityX-21 MP digital camera mounted atop the microscope.

1.6. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed on a Mettler DSC822e fitted with an autosampler operating with Mettler Star software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg⁻¹) under an atmosphere of dry nitrogen.

1.7. Small Angle X-ray Scattering (SAXS)

Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. The radiation used was copper Kα (λ = 0.154056 nm) from a 1 μS microfocus source. A silver behenate standard was used to calibrate d-spacings and determine instrumental broadening. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample. Samples were filled into 0.9 mm O.D. capillary tubes (approx. I.D. ~0.85 mm) and aligned with a pair of 1T magnets, with the field strength at the sample position being approximately 0.6T. Diffraction patterns were collected as a function of temperature and the data processed using Matlab as follows. Two-dimensional scattering patterns were collected on cooling from the isotropic liquid until crystallisation in ~ 1.2 °C intervals. These were radially averaged (0.05 ° step size) to give scattered intensity as a function of 2θ for each frame. Fitting of this integrated data with a Voigt function (in all cases R² > 0.99) allowed the peak position and FWHM to be determined for both the small- and wide-angle peaks; the FWHM was corrected for instrumental broadening then used to determine correlation lengths parallel and perpendicular to the director. FWHM and d-spacing values were converted into 2θ allowing us to obtain domain sizes from the Scherrer equation. All data processing was carried out using custom Matlab scripts which may be made available on request from the corresponding author.
1.8. **Computational Chemistry**

Quantum chemical calculations were performed using the Gaussian 09 revision e.01 suite of programmes. [1]

1.9. **Single Crystal X-ray Diffraction**

Single-crystal diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-Kα radiation (λ = 1.54184 Å) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with “Crysalis”. [2] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. [3] OLEX2 [4] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for structure solution were Superflip charge-flipping” [5] for 10 and “ShelXT dual-space” [6] for 14. Refinement by full-matrix least-squares used the SHELXL-97 [7] algorithm within OLEX2. [4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions. Both structures exhibited disorder of the branched alkyl chain. For 10, the 2,4,4-trimethylpentanol group was disordered and modelled in two positions with refined occupancies of 0.766:0.234(3), the ADP of the disordered atom pairs were constrained to be the same. For 14, the 3,5,5-trimethylhexanol group was disorder and modelled in two positions with refined occupancies of 0.731:0.269(4). The C_{22}-O_{3} and C_{22}-O_{3a} bond lengths were restrained to be equal, C_{22a}-C_{23a} was restrained to be 1.52 angstroms and the ADP of C_{22} and C_{22a} constrained to be equal.
Scheme 1

\[ \text{HO} - \text{C} - \text{O} + \underset{n=1}{\text{2}} \quad \text{HO} - \text{C} - \text{O} \quad \text{THF, N}_2 \quad \text{EDAC, DMAP, DCM, N}_2 \quad \underset{R''}{\text{HO}} \]

\[ \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{O} \quad \text{KOH, EtOH, H}_2\text{
1.2. Synthetic Details and Chemical Characterisation

4-(2,4,4-Trimethylpentyloxy)benzoic acid (4)

To a stirred solution of 2,4,4-trimethylpentan-1-ol (5 g, 38.46 mmol), triphenyl phosphine (10.1 g, 38.46 mmol) and methyl 4-hydroxybenzoate (6.4 g, 42.31 mmol) in anhydrous THF (125 ml), under an atmosphere of dry nitrogen, was added neat DIAD (7.8 g, 7.6 ml, 38.46 mmol) dropwise over a period of 0.5h. The resulting solution was stirred for 6h, and the solvent removed in vacuo. Ethanol (100 ml) was added to the crude residue and the solution was heated under reflux before the addition of 4M sodium hydroxide solution (30 ml). The solution was heated under reflux for 16 h, cooled to r.t. and diluted with water (100 ml) and filtered. The filtrate was acidified to pH 1 with 36% HCl, the resulting precipitate collected by filtration and recrystallised from ethanol giving the title compound as translucent needles.

Yield: 7.4 g (73%)

Melting Point: 106.3 °C

^1H NMR (400 MHz, CDCl3): 0.79 (9H, S), 0.88 (3H, d, J_{HH} = 6.4 Hz), 0.94 – 1.03 (1H, m), 1.17 – 1.24 (1H, m), 1.42 – 1.54 (1H, m), 1.58 – 1.68 (2H, m), 3.96 (2H, t, J_{HH} = 6.4), 6.90 (2H, ddd, J_{HH} = 2.1 Hz, J_{HH} = 2.8 Hz, J_{HH} = 8.9 Hz), 7.80 (2H, ddd, J_{HH} = 2.1 Hz, J_{HH} = 2.8 Hz, J_{HH} = 8.9 Hz).

MS M/Z (ESI+): 273.1462 (C_{15}H_{22}NaO_{3}, calcd. for C_{15}H_{23}O_{3}: 273.1461, M+Na), 251.1650 (C_{15}H_{23}O_{3}, calcd. for C_{15}H_{23}O_{3}: 251.1642, M+H)

FT-IR (v max, cm⁻¹): 547, 640, 771, 840, 941, 1026, 1118, 1157, 1249, 1296, 1427, 1604, 1674, 2553, 2669, 2826, 2947
4-(3,5,5-Trimethylhexyloxy)benzoic acid (5)

Quantities used: 3,5,5-Trimethylhexan-1-ol (15 g, 18.2 ml, 0.113 mol), methyl 4-hydroxybenzoate (17 g, 0.112 mol), PPh₃ (27.9 g, 0.106 mol), DIAD (21.5 g, 0.106 mol), THF (200 ml), then aqueous 4M NaOH (100 ml), EtOH (300 ml). The experimental procedure was as described in the synthesis of compound 4, giving the title compound as white plates.

Yield: 19.7 g (76%)

Melting Point: 122.2 °C

¹H NMR (400 MHz, DMSO-D6): 0.79 (9H, s), 0.88 (3H, d, J₆₋₇ = 6.4 Hz), 0.94 – 1.03 (1H, m Hz), 1.17 – 1.24 (1H, m), 1.42 – 1.54 (1H, M), 1.58 – 1.68 (2H, m), 3.96 (2H, t, J₆₋₇ = 6.4 Hz), 6.90 (2H, ddd, J₆₋₇ = 2.1 Hz, J₆₋₇ = 2.8 Hz, J₆₋₇ = 8.9 Hz), 7.80 (2H, ddd, J₆₋₇ = 2.1 Hz, J₆₋₇ = 2.8 Hz, J₆₋₇ = 8.9 Hz)

MS M/Z (ESI+): 287.1609 (C₁₆H₂₄NaO₃, calcd. for C₁₆H₂₄NaO₃: 287.1618, M + Na), 265.1787 (C₁₆H₂₃O₃, calcd. for C₁₆H₂₃O₃: 265.1798, M + H)

FT-IR (v max, cm⁻¹): 503, 553, 632, 650, 693, 763, 771, 827, 844, 889, 943, 968, 997, 1012, 1053, 1109, 1128, 1166, 1201, 1251, 1296, 1321, 1363, 1390, 1429, 1473, 1514, 1579, 1604, 1674, 2868, 2895, 2953
**4-(4-Ethylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (10)**

Compound 4 (400 mg, 1.6 mmol), compound 6 (391 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol) were dissolved into dry DCM (4 ml) in an oven dried vial, and the resulting solution stirred for 16h. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (10:1) to give the title compound as white needles.

Yield: 0.47 g (67%)

$^1$H NMR (400 MHz, CDCl₃): 0.81 – 1.42 (22H, m), 1.77 – 1.87 (4H, m), 1.89 – 2.01 (1H, m), 2.41 (1H, tt, $J_{HH} = 3.1$ Hz, $J_{HH} = 12.4$ Hz), 3.66 (1H, dd, $J_{HH} = 7.3$ Hz, $J_{HH} = 8.9$ Hz), 3.77 (1H, dd, $J_{HH} = 5.8$ Hz, $J_{HH} = 8.9$ Hz), 6.87 (2H, ddd, $J_{HH} = 1.8$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.5$ Hz), 7.02 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.5$ Hz), 8.06 (2H, ddd, $J_{HH} = 1.8$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.9$ Hz)

$^{13}$C($^1$H) NMR (100.5 MHz, CDCl₃): 11.53, 19.93, 29.50, 29.85, 29.95, 33.12, 34.37, 39.03, 44.07, 47.28, 74.34, 114.23, 121.36, 121.65, 127.70, 132.19, 145.21, 148.94, 163.51, 165.12

MS M/Z (ESI+): 475.2608 (C$_{29}$H$_{40}$KO$_3$, calcd. for C$_{29}$H$_{40}$KO$_3$: 475.2609, M + K) 459.2860 (C$_{29}$H$_{40}$NaO$_3$, calcd. for C$_{29}$H$_{40}$NaO$_3$: 459.2870, M + Na) 437.3036 (C$_{29}$H$_{21}$O$_3$, calcd. for C$_{29}$H$_{21}$O$_3$: 437.3050, M + H)

FT-IR (v max, cm⁻¹): 516, 542, 605, 630, 659, 690, 763, 802, 844, 877, 939, 968, 1004, 1074, 1105, 1166, 1201, 1257, 1317, 1446, 1465, 1510, 1604, 1720, 2848, 2870, 2891, 2918, 2953.

Assay (RP-HPLC): 99.3%
4-(4-Propylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (11)

Quantities used: 4 (400 mg, 1.6 mmol), compound 7 (418 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (17:1) to give the title compound as white needles.

Yield: 0.38 g (52%)

$^1$H NMR (400 MHz, CDCl$_3$): 0.82 (3H, t, $J_{HH} = 7.0$ Hz), 0.86 (9H, s), 0.89 – 1.41 (12H, m), 1.75 – 1.87 (4H, m), 1.89 – 2.01 (1H, m), 2.40 (1H, tt, $J_{HH} = 3.4$ Hz, $J_{HH} = 12.2$ Hz), 3.65 (1H, dd, $J_{HH} = 7.3$ Hz, $J_{HH} = 9.2$ Hz), 3.77 (1H, dd, $J_{HH} = 5.8$ Hz, $J_{HH} = 9.2$ Hz), 6.87 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.9$ Hz), 7.03 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.9$ Hz), 7.16 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.9$ Hz), 8.05 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.9$ Hz)

$^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$): 14.40, 19.92, 20.01, 29.50, 29.85, 30.96, 33.51, 34.38, 36.96, 39.68, 44.06, 47.28, 74.34, 114.22, 121.36, 121.65, 127.69, 132.19, 145.21, 148.93, 163.51, 165.11

MS M/Z (ESI+): 489.2758 (C$_{30}$H$_{42}$KO$_3$, calcld. for C$_{30}$H$_{42}$KO$_3$: 489.2766, M + K)
473.3020 (C$_{30}$H$_{42}$NaO$_3$, calcld. for C$_{30}$H$_{42}$NaO$_3$: 473.3026, M + Na)

FT-IR (v max, cm$^{-1}$): 513, 536, 605, 632, 661, 692, 763, 800, 842, 875, 970, 1012, 1026, 7076, 1165, 1205, 1251, 1313, 1363, 1446, 1467, 1510, 1602, 1720, 2848, 2891, 2954.

Assay (RP-HPLC): 99.9%
4-(4-Butylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (12)

Quantities used: 4 (400 mg, 1.6 mmol), compound 8 (445 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

Yield: 0.26 g (35%)

$^1$H NMR (400 MHz, CDCl$_3$): 0.80 – 1.42 (26H, m), 1.76 – 1.88 (4H, m), 1.90 – 2.00 (1H, m), 2.41 (1H, tt, $J_{H-H}$ = 3.4 Hz, $J_{H-H}$ = 12.4 Hz), 3.66 (1H, dd, $J_{H-H}$ = 7.3 Hz, $J_{H-H}$ = 9.2 Hz), 3.77 (1H, dd, $J_{H-H}$ = 6.1 Hz, $J_{H-H}$ = 9.2 Hz), 6.88 (2H, ddd, $J_{H-H}$ = 1.8 Hz, $J_{H-H}$ = 3.1 Hz, $J_{H-H}$ = 8.9 Hz), 7.03 (2H, ddd, $J_{H-H}$ = 2.1 Hz, $J_{H-H}$ = 2.8 Hz, $J_{H-H}$ = 8.5 Hz), 7.18 (2H, ddd, $J_{H-H}$ = 2.1 Hz, $J_{H-H}$ = 2.8 Hz, $J_{H-H}$ = 8.5 Hz), 8.05 (2H, ddd, $J_{H-H}$ = 1.8 Hz, $J_{H-H}$ = 3.1 Hz, $J_{H-H}$ = 8.9 Hz)

$^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$): 14.16, 19.93, 23.00, 29.22, 29.51, 29.86, 30.97, 33.56, 34.40, 37.08, 37.24, 44.07, 47.29, 74.35, 114.23, 121.36, 121.65, 127.70, 132.19, 145.23, 148.94, 163.51, 165.12

MS M/Z (ESI+): 487.3168 (C$_{31}$H$_{44}$NaO$_3$, cacld. for C$_{31}$H$_{44}$NaO$_3$: 487.6792, M + Na), 465.3353 (C$_{31}$H$_{45}$O$_3$, cacld. for C$_{31}$H$_{45}$O$_3$: 465.6975, M + H)

FT-IR ($\nu$ max, cm$^{-1}$): 511, 538, 607, 632, 661, 692, 763, 800, 846, 877, 975, 1016, 1066, 1165, 1195, 1253, 1317, 1361, 1465, 1510, 1602, 1724, 2852, 2918, 2954.

Assay (RP-HPLC): 99.9%
4-(4-Pentylcyclohexyl)phenyl 4-((2,4,4-trimethylpentyl)oxy)benzoate (13)

Quantities used: 4 (400 mg, 1.6 mmol), compound 9 (472 mg, 1.92 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

Yield: 0.66 g (87%)

$^1$H NMR (400 MHz, CDCl$_3$): 0.80 – 1.42 (28H, m), 1.75 – 1.87 (4H, m), 1.89 – 2.00 (1H, m), 2.40 (1H, tt, $J_{HH} = 3.0$ Hz, $J_{HSH} = 12.1$ Hz), 3.65 (1H, dd, $J_{HH} = 7.3$ Hz, $J_{HH} = 8.9$ Hz), 3.75 (1H, dd, $J_{HH} = 6.1$ Hz, $J_{HSH} = 8.9$ Hz), 6.87 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.9$ Hz), 7.02 (2H, ddd, $J_{HH} = 1.8$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.5$ Hz), 7.18 (2H, ddd, $J_{HH} = 1.8$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.5$ Hz), 8.06 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.8$ Hz, $J_{HH} = 8.9$ Hz)

$^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$): 14.12, 19.92, 22.70, 26.63, 29.50, 29.86, 30.96, 32.19, 33.56, 34.40, 37.26, 37.35, 44.07, 47.29, 74.34, 114.23, 121.36, 121.65, 127.69, 132.19, 145.21, 148.94, 163.51, 165.10

MS M/Z (ESI+): 501.3320 (C$_{32}$H$_{46}$NaO$_3$, caclld. for C$_{32}$H$_{46}$NaO$_3$: 501.3339, M + Na)

479.3515 (C$_{32}$H$_{47}$O$_3$, caclld. for C$_{32}$H$_{47}$O$_3$: 479.7245, M + H)

FT-IR (v max, cm$^{-1}$): 538, 607, 632, 692, 763, 800, 846, 877, 1016, 1066, 1165, 1195, 1253, 1317, 1361, 1465, 1510, 1602, 1724, 2852, 2954.

Assay (RP-HPLC): 99.9%
4-(4-Ethylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (14)

Quantities used: 5 (200 mg, 0.77 mmol), compound 6 (160 mg, 0.77 mmol), EDAC (170 mg, 0.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

Yield:
300 mg (87%)

$^1$H NMR (400 MHz, CDCl$_3$):
0.90 (9H, s), 0.99 (2H, d, $J_{	ext{H-H}} = 6.7$ Hz), 1.31 – 1.01 (5H, m), 1.54 – 1.38 (2H, m), 1.66 (1H, quint, $J_{	ext{H-H}} = 6.4$ Hz), 1.94 – 1.71 (6H, m), 2.48 (1H, tt, $J_{	ext{H-H}} = 3.1$ Hz, $J_{	ext{H-H}} = 12.2$ Hz), 4.05 (2H, t, $J_{	ext{H-H}} = 6.4$ Hz), 6.96 (2H, ddd, $J_{	ext{H-H}} = 2.1$ Hz, $J_{	ext{H-H}} = 2.4$ Hz, $J_{	ext{H-H}} = 8.9$ Hz), 7.09 (2H, ddd, $J_{	ext{H-H}} = 1.8$ Hz, $J_{	ext{H-H}} = 2.4$ Hz, $J_{	ext{H-H}} = 8.5$ Hz), 7.23 (2H, ddd, $J_{	ext{H-H}} = 1.8$ Hz, $J_{	ext{H-H}} = 2.4$ Hz, $J_{	ext{H-H}} = 8.5$ Hz), 8.12 (2H, ddd, $J_{	ext{H-H}} = 2.1$ Hz, $J_{	ext{H-H}} = 2.4$ Hz, $J_{	ext{H-H}} = 8.9$ Hz)

$^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$):
11.53, 22.76, 26.08, 29.92, 29.95, 31.13, 33.12, 34.36, 38.25, 39.02, 44.07, 51.02, 66.52, 114.20, 121.35, 121.67, 127.70, 132.20, 145.22, 148.93, 163.38, 165.13

MS M/Z (ESI+):
473.3019 (C$_{30}$H$_{42}$NaO$_3$, calcd. for C$_{30}$H$_{42}$NaO$_3$: 473.3026, M + Na)
451.3183 (C$_{30}$H$_{32}$O$_3$, calcd. for C$_{30}$H$_{32}$O$_3$: 451.6705, M + H)

FT-IR ($\nu$ max, cm$^{-1}$):
501, 540, 601, 655, 763, 972, 1072, 1165, 1257, 1465, 1512, 1581, 1604, 1728, 2846, 2908, 2954

Assay (RP-HPLC):
98.6%
**4-(4-Propylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (15)**

Quantities used: 5 (200 mg, 0.77 mmol), compound 7 (160 mg, 0.77 mmol), EDAC (170 mg, 0.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

**Yield:** 320 mg (89%)

**1H NMR (400 MHz, CDCl₃):**

- 0.93 – 0.85 (12H, m), 0.99 (2H, d, J₆₉ = 6.6 Hz), 1.54 – 1.02 (5H, m), 1.93 – 1.60 (7H, m), 2.47 (1H, tt, J₆₉ = 3.3 Hz, J₉₉ = 12.1 Hz), 4.05 (2H, t, J₆₉ = 6.6 Hz Hz), 6.95 (2H, ddd, J₆₉ = 1.8 Hz, J₉₉ = 2.8 Hz, J₉₉ = 8.8 Hz), 7.09 (2H, ddd, J₆₉ = 1.8 Hz, J₉₉ = 2.4 Hz, J₉₉ = 8.5 Hz), 7.23 (2H, ddd, J₉₉ = 1.8 Hz, J₉₉ = 2.4 Hz, J₉₉ = 8.5 Hz), 8.12 (2H, ddd, J₆₉ = 1.8 Hz, J₉₉ = 2.8 Hz, J₉₉ = 8.8 Hz).

**13C{¹H} NMR (100.5 MHz, CDCl₃):**

- 14.40, 20.01, 22.76, 26.08, 29.92, 31.13, 33.52, 34.39, 36.96, 38.25, 39.68, 44.07, 51.02, 66.52, 114.19, 121.36, 121.68, 127.70, 132.20, 145.23, 148.93, 163.38, 165.12

**MS M/Z (ESI+):**

- 465.3379 (C₃₀H₄₅O₃, cacld. for C₃₀H₄₅O₃: 465.3363, M + H)

**FT-IR (v max, cm⁻¹):**

- 540, 609, 655, 686, 763, 848, 972, 1010, 1072, 1165, 1195, 1257, 1465, 1512, 1581, 1604, 1720, 2846, 2916

**Assay (RP-HPLC):** 99.7%
4-(4-Butylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (16)

Quantities used: 5 (200 mg, 0.77 mmol), compound 8 (170 mg, 0.77 mmol), EDAC (170 mg, 0.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (14:1) to give the title compound as white needles.

Yield: 310 mg (84%)

$^1$H NMR (400 MHz, CDCl$_3$): 0.99 (2H, d, $J_{HH} = 6.6$ Hz), 0.89 (12H, s), 1.11 (1H, d, $J_{HH} = 5.5$), 1.14 (1H, d, $J_{HH} = 5.9$ Hz), 1.32 – 1.20 (8H, m), 1.54 – 1.37 (3H, m), 1.65 (1H, quint, $J_{HH} = 6.6$ Hz), 1.93 – 1.70 (6H, m), 2.52 – 2.42 (1H, t, $J_{HH} = 2.9$ Hz, $J_{HH} = 12.2$ Hz), 4.05 (2H, t, $J_{HH} = 6.6$ Hz), 6.96 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.8$ Hz), 7.09 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.5$ Hz), 7.23 (2H, ddd $J_{HH} = 2.1$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.8$ Hz), 8.12 (2H, ddd, $J_{HH} = 2.1$ Hz, $J_{HH} = 2.4$ Hz, $J_{HH} = 8.8$ Hz).

$^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$): 14.16, 22.76, 23.00, 26.08, 29.22, 29.92, 31.13, 33.56, 34.40, 37.08, 37.24, 38.25, 44.07, 51.02, 66.52, 114.20, 121.36, 121.67, 127.70, 132.20, 145.23, 148.93, 163.38, 165.12

MS M/Z (ESI+): 479.2757 (C$_{30}$H$_{47}$O$_3$, cacld. for C$_{30}$H$_{47}$O$_3$: 479.7245, M + H)

FT-IR ($\nu$ max, cm$^{-1}$): 501, 540, 663, 686, 763, 810, 848, 871, 1010, 1072, 1165, 1195, 1257, 1465, 1512, 1604, 1720, 2846, 2916

Assay (RP-HPLC): 98.1%
4-(4-Pentylcyclohexyl)phenyl 4-((3,5,5-trimethylhexyl)oxy)benzoate (17)

Quantities used: 5 (400 mg, 1.6 mmol), compound 9 (377 mg, 1.6 mmol), EDAC (367 mg, 1.92 mmol), DMAP (10 mg, 82 µmol), DCM (4 ml). The experimental procedure was as described in the synthesis of compound 10. The crude material was purified by flash chromatography with DCM as the eluent and recrystallised from ethanol/THF (15:1) to give the title compound as white needles.

Yield: 0.55 g (70%)

1H NMR (400 MHz, CDCl3): 0.77 – 1.90 (35H, m), 2.41 (1H, tt, J_H-H = 3.1 Hz, J_H-H = 12.2 Hz), 3.98 (2H, t, J_H-H = 7.0 Hz), 6.89 (2H, ddd, J_H-H = 1.8 Hz, J_H-H = 2.6 Hz, J_H-H = 9.2 Hz), 7.03 (2H, ddd, J_H-H = 2.1 Hz, J_H-H = 2.4 Hz, J_H-H = 8.8 Hz), 7.17 (2H, ddd, J_H-H = 2.1 Hz, J_H-H = 2.4 Hz, J_H-H = 8.8 Hz), 8.06 (2H, ddd, J_H-H = 1.8 Hz, J_H-H = 2.6 Hz, J_H-H = 9.2 Hz).

13C{1H} NMR (100.5 MHz, CDCl3): 14.12, 22.70, 22.76, 26.07, 26.63, 29.91, 31.12, 32.19, 33.55, 34.39, 37.25, 37.35, 38.25, 44.06, 51.01, 66.51, 114.19, 121.35, 121.67, 127.68, 132.19, 145.21, 148.93, 163.38, 165.10

MS M/Z (ESI+): 515.3480 (C_{33}H_{48}NaO_3, calcd. for C_{33}H_{48}NaO_3: 515.3496, M + Na), 493.3657 (C_{33}H_{46}O_3, calcd. for C_{33}H_{46}O_3: 493.3676, M + H)

FT-IR (ν max, cm⁻¹): 501, 663, 686, 763, 810, 848, 1010, 1072, 1165, 1195, 1257, 1465, 1512, 1604, 1720, 2846, 2916

Assay (RP-HPLC): 99.9%
2. Supplemental Figures

2.1. Supplemental SAXS Data

Figure SI-1: The nematic phase of compound 13 as studied by SAXS. (a-g), evolution of the small-angle scattering peak for a magnetically aligned sample of 13 as a function of the indicated reduced temperartures, and (h) plot of integrated diffraction intensity for the small angle peak as a function of the angle $\chi$ for compound 13 at three different reduced temperatures.
2.2. Supplemental Single Crystal X-ray Diffraction Data

Figure SI-2: Thermal ellipsoid model (50% probability level) of the structure of (a) compound 10 and (b) compound 14 obtained by X-ray diffraction on single crystals grown from neat ethanol with a thermal gradient. For 10 the angle between the plane of the two phenyl rings is 58.76(9) °, and for 14 it is 58.18(2) °. For 10 the plane of the major form of the bulky end group (mean of 25 atoms) is at an angle of 84.59(6)° from the plane of the mesogenic unit (mean of 46 atoms) while for 14 the end group (mean of 28 atoms) is at an angle of 80.96(6) ° from the plane of the mesogenic unit (mean of 46 atoms).
2.3. Supplemental Mixture Data

Figure SI-3: Transition temperatures (°C) of binary mixtures of 17 with *bis* decylterephthalaniline (TBDA)
2.2. Supplemental XRD data

2.2.1. Structure 10

![Structure 10](image)

Table 1: Crystal data and structure refinement for 10.

| Identification code | jwg1609       |
|---------------------|---------------|
| Empirical formula   | C$_{29}$H$_{40}$O$_{3}$ |
| Formula weight      | 436.61        |
| Temperature/K       | 109.9(2)      |
| Crystal system      | monoclinic    |
| Space group         | P2$_1$/c      |
| a/Å                 | 16.7608(8)    |
| b/Å                 | 5.5364(2)     |
| c/Å                 | 28.2495(12)   |
| α/°                 | 90            |
| β/°                 | 106.554(5)    |
| γ/°                 | 90            |
| Volume/Å$^3$        | 2512.7(2)     |
| Z                   | 4             |
| ρ calc/g/cm$^3$     | 1.154         |
| μ/mm$^{-1}$         | 0.564         |
| F(000)              | 952.0         |
| Crystal size/mm$^3$ | 0.251 × 0.075 × 0.046 |
| Radiation           | CuKα (λ = 1.54184) |
2θ range for data collection/° 7.242 to 142.068

Index ranges
-15 ≤ h ≤ 20, -6 ≤ k ≤ 5, -34 ≤ l ≤ 34

Reflections collected 10843

Independent reflections 4772 [R_{int} = 0.0504, R_{sigma} = 0.0493]

Data/restraints/parameters 4772/0/306

Goodness-of-fit on F^2 1.056

Final R indexes [I>=2σ (I)] R_{1} = 0.0743, wR_{2} = 0.1900

Final R indexes [all data] R_{1} = 0.0951, wR_{2} = 0.2121

Largest diff. peak/hole / e Å^{-3} 0.35/-0.37

Table 2 Bond Lengths for 10.

| Atom | Atom | Length/Å |
|------|------|----------|
| O1   | C12  | 1.413(2) |
| O1   | C15  | 1.366(3) |
| O2   | C15  | 1.203(3) |
| C1   | C2   | 1.512(4) |
| C2   | C3   | 1.520(3) |
| C3   | C4   | 1.519(3) |
| C3   | C8   | 1.527(3) |
| C4   | C5   | 1.532(3) |
| C5   | C6   | 1.532(3) |
| C6   | C7   | 1.535(3) |
| C6   | C9   | 1.515(3) |
| C7   | C8   | 1.521(3) |
| C9   | C10  | 1.386(3) |
| C9   | C14  | 1.395(3) |
| Atom | Atom | Atom | Angle/°          |
|------|------|------|-----------------|
| C15  | O1   | C12  | 117.82(18)      |
| C1   | C2   | C3   | 115.0(2)        |
| C2   | C3   | C8   | 112.70(19)      |
| C4   | C3   | C2   | 111.4(2)        |
| C4   | C3   | C8   | 109.83(19)      |
| C3   | C4   | C5   | 112.7(2)        |
| C6   | C5   | C4   | 111.39(19)      |
| C5   | C6   | C7   | 109.71(18)      |
| C9   | C6   | C5   | 112.47(18)      |
| C9   | C6   | C7   | 112.76(19)      |
| C8   | C7   | C6   | 111.9(2)        |
| C7   | C8   | C3   | 112.21(19)      |
| C10  | C9   | C6   | 120.3(2)        |
| C10  | C9   | C14  | 118.0(2)        |
| C14  | C9   | C6   | 121.6(2)        |
| C9   | C10  | C11  | 121.5(2)        |
| C12  | C11  | C10  | 118.4(2)        |
| C11  | C12  | O1   | 116.7(2)        |
| C13  | C12  | O1   | 121.4(2)        |

Table 3 Bond Angles for 10.

| Atom | Atom | Angle/°          |
|------|------|-----------------|
| O3   | C22  | 1.440(4)        |
| C22  | C23  | 1.516(4)        |
| C23  | C24  | 1.538(4)        |
| O3A  | C22A | 1.430(14)       |
| C22A | C23A | 1.527(12)       |
| C23A | C24A | 1.499(15)       |
C13  C12  C11  121.8(2)  C22  C23  C29  110.3(2)
C12  C13  C14  119.0(2)  C22  C23  C24  115.1(2)
C13  C14  C9  121.3(2)  C24  C23  C29  108.4(3)
O1  C15  C16  111.1(2)  C23  C24  C25  119.9(3)
O2  C15  O1  123.1(2)  C19  O3A  C22A  108.7(8)
O2  C15  C16  125.8(2)  O3A  C22A  C23A  107.7(9)
C17  C16  C15  122.2(2)  C29  C23A  C22A  110.0(7)
C21  C16  C15  119.0(2)  C24A  C23A  C29  110.6(7)
C21  C16  C17  118.8(2)  C24A  C23A  C22A  117.6(9)
C18  C17  C16  120.2(2)  C23A  C24A  C25  118.5(8)

Table 4 Torsion Angles for 10.

| A   | B   | C   | D   | Angle/°  | A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|----------|-----|-----|-----|-----|----------|
| O1  | C12 | C13 | C14 | 178.2(2) | C15 | O1  | C12 | C13 | 69.2(3)  |
| O1  | C15 | C16 | C17 | -7.3(3)  | C15 | C16 | C17 | C18 | -179.5(2) |
| O1  | C15 | C16 | C21 | 173.47(19) | C15 | C16 | C21 | C20 | 179.6(2) |
| O2  | C15 | C16 | C17 | 172.7(2) | C16 | C17 | C18 | C19 | -0.3(3)  |
| O2  | C15 | C16 | C21 | -6.5(3)  | C17 | C16 | C21 | C20 | 0.4(3)   |
| C1  | C2  | C3  | C4  | -172.2(2) | C17 | C18 | C19 | C20 | 0.7(3)   |
| C1  | C2  | C3  | C8  | 63.8(3)  | C17 | C18 | C19 | O3  | -179.9(2) |
| C2  | C3  | C4  | C5  | 179.85(19) | C17 | C18 | C19 | O3A | -179.6(8) |
| C2  | C3  | C8  | C7  | 179.5(2) | C18 | C19 | C20 | C21 | -0.5(3)  |
| C3  | C4  | C5  | C6  | 55.9(3)  | C18 | C19 | O3  | C22 | 179.3(2) |
| C4  | C3  | C8  | C7  | 54.6(3)  | C18 | C19 | O3A | C22A| 1.1(13)  |
| C4  | C5  | C6  | C7  | -54.7(3) | C19 | C20 | C21 | C16 | 0.0(3)   |
| C4  | C5  | C6  | C9  | 178.9(2) | C19 | O3  | C22 | C23 | 175.7(3) |
| C5  | C6  | C7  | C8  | 55.4(3)  | C19 | O3A | C22A| C23A| -174.3(8) |
| C5  | C6  | C9  | C10 | -107.7(2) | C20 | C19 | O3  | C22 | -1.3(4)  |
| C5  | C6  | C9  | C14 | 71.3(3) | C20 | C19 | O3A | C22A | -179.1(7) |
|-----|-----|-----|-----|---------|-----|-----|-----|------|-----------|
| C6  | C7  | C8  | C3  | -56.3(3)| C21 | C16 | C17 | C18  | -0.3(3)   |
| C6  | C9  | C10 | C11 | -179.0(2)| C26 | C25 | C24 | C23  | 57.4(3)   |
| C6  | C9  | C14 | C13 | 178.8(2)| C26 | C25 | C24A| C23A | -161.4(8) |
| C7  | C6  | C9  | C10 | 127.6(2)| C27 | C25 | C24 | C23  | 173.8(2)  |
| C7  | C6  | C9  | C14 | -53.4(3)| C27 | C25 | C24A| C23A | -50.7(10) |
| C8  | C3  | C4  | C5  | -54.6(3)| C28 | C25 | C24 | C23  | -69.5(3)  |
| C9  | C6  | C7  | C8  | -178.44(18)| C28 | C25 | C24A| C23A | 88.5(8)   |
| C9  | C10 | C11 | C12 | 0.4(3)  | C29 | C23 | C24 | C25  | -162.0(2) |
| C10 | C9  | C14 | C13 | -2.2(3) | C29 | C23A| C24A| C25  | 167.2(6)  |
| C10 | C11 | C12 | O1  | -178.60(19)| O3  | C19 | C20 | C21  | -179.9(3) |
| C10 | C11 | C12 | C13 | -2.6(3) | O3  | C22 | C23 | C29  | -69.9(3)  |
| C11 | C12 | C13 | C14 | 2.4(3)  | O3  | C22 | C23 | C24  | 53.1(4)   |
| C12 | O1  | C15 | O2  | -3.1(3) | C22 | C23 | C24 | C25  | 74.0(3)   |
| C12 | O1  | C15 | C16 | 176.91(18)| O3A | C19 | C20 | C21  | 179.6(6)  |
| C12 | C13 | C14 | C9  | 0.0(3)  | O3A | C22A| C23A| C29  | 69.6(11)  |
| C14 | C9  | C10 | C11 | 1.9(3)  | O3A | C22A| C23A| C24A | -58.2(12) |
| C15 | O1  | C12 | C11 | -114.8(2)| C22A|C23A|C24A|C25  | -65.3(12) |
Table 1 Crystal data and structure refinement for 14.

| Property                     | Value                  |
|------------------------------|------------------------|
| Identification code          | jwg1608                |
| Empirical formula            | C₃₀H₄₂O₃               |
| Formula weight               | 450.63                 |
| Temperature/K                | 110.05(10)             |
| Crystal system               | monoclinic             |
| Space group                  | P2₁/n                  |
| a/Å                          | 16.3302(6)             |
| b/Å                          | 5.5649(2)              |
| c/Å                          | 29.6423(9)             |
| α/°                          | 90                     |
| β/°                          | 104.367(3)             |
| γ/°                          | 90                     |
| Volume/Å³                    | 2609.53(16)            |
| Z                            | 4                      |
\( \rho_{\text{calc}} \text{g/cm}^3 \) 1.147
\( \mu/\text{mm}^{-1} \) 0.557
F(000) 984.0
Crystal size/mm\(^3\) 0.433 \times 0.088 \times 0.038
Radiation CuK\( \alpha \) (\( \lambda = 1.54184 \))
2\( \theta \) range for data collection/° 9.54 to 134.106
Index ranges \(-19 \leq h \leq 14, -6 \leq k \leq 6, -26 \leq l \leq 35\)
Reflects collected 9357
Independent reflections 4663 [R\(_{\text{int}}\) = 0.0319, R\(_{\text{sigma}}\) = 0.0346]
Data/restraints/parameters 4663/2/348
Goodness-of-fit on F\(^2\) 1.087
Final R indexes [I\( \geq 2\sigma (I)\)] \( R_1 = 0.0683, wR_2 = 0.1701 \)
Final R indexes [all data] \( R_1 = 0.0807, wR_2 = 0.1793 \)
Largest diff. peak/hole / e Å\(^3\) 0.26/-0.38

**Table 2 Bond Lengths for 14**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C1   | C2   | 1.522(4) | C17  | C18  | 1.394(3) |
| C2   | C3   | 1.532(3) | C18  | C19  | 1.384(3) |
| C3   | C4   | 1.517(3) | C19  | C20  | 1.390(4) |
| C3   | C8   | 1.529(3) | C19  | O3   | 1.370(3) |
| C4   | C5   | 1.525(3) | C20  | C21  | 1.374(4) |
| C5   | C6   | 1.533(3) | C22  | C23  | 1.539(8) |
| C6   | C7   | 1.530(3) | C22  | O3   | 1.457(5) |
| C6   | C9   | 1.510(3) | C22A | C23A | 1.523(18) |
| C7   | C8   | 1.524(3) | C22A | O3   | 1.439(9) |
| C9   | C10  | 1.390(3) | C23  | C24  | 1.536(6) |
| C9   | C14  | 1.397(3) | C23A | C24A | 1.505(13) |
Table 3 Bond Angles for 14.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C1   | C2   | C3   | 114.6(2)| C18  | C19  | C20  | 120.0(2)|
| C4   | C3   | C2   | 110.73(19)| O3   | C19  | C18  | 124.5(2)|
| C4   | C3   | C8   | 109.77(19)| O3   | C19  | C20  | 115.5(2)|
| C8   | C3   | C2   | 112.98(18)| C21  | C20  | C19  | 120.0(2)|
| C3   | C4   | C5   | 113.2(2)  | C20  | C21  | C16  | 120.9(2)|
| C4   | C5   | C6   | 111.45(19)| O3   | C22  | C23  | 110.9(5)|
| C7   | C6   | C5   | 109.53(19)| O3   | C22A | C23A | 92.9(9) |
| C9   | C6   | C5   | 112.21(18)| C24  | C23  | C22  | 116.8(4)|
| C9   | C6   | C7   | 113.32(19)| C24A | C23A | C22A | 101.6(7)|
| C8   | C7   | C6   | 111.8(2)  | C23  | C24  | C30  | 107.1(4)|
| C7   | C8   | C3   | 112.02(18)| C25  | C24  | C23  | 110.1(4)|
| C10  | C9   | C6   | 120.6(2)  | C25  | C24  | C30  | 111.1(3)|
| C10  | C9   | C14  | 117.8(2)  | C23A | C24A | C25A | 114.4(10)|
| C14  | C9   | C6   | 121.6(2)  | C23A | C24A | C30A | 110.7(9) |
| C11  | C10  | C9   | 121.8(2)  | C25A | C24A | C30A | 109.2(7) |
| A   | B   | C   | D   | Angle/°       | A   | B   | C   | D   | Angle/°       |
|-----|-----|-----|-----|--------------|-----|-----|-----|-----|--------------|
| C1  | C2  | C3  | C4  | 176.1(2)     | C1  | C17 | C18 | C19 | -179.9(2)    |
| C1  | C2  | C3  | C8  | -60.3(3)     | C18 | C19 | C20 | C21 | 0.2(4)       |
| C2  | C3  | C4  | C5  | 179.4(2)     | C18 | C19 | C3  | C22 | 5.5(4)       |
| C2  | C3  | C8  | C7  | -178.4(2)    | C18 | C19 | C3  | C22A| -9.8(12)    |
| C3  | C4  | C5  | C6  | -55.5(3)     | C19 | C20 | C21 | C16 | -0.3(4)      |
| C4  | C3  | C8  | C7  | -54.2(3)     | C20 | C19 | C3  | C22 | -174.2(3)    |
| C4  | C5  | C6  | C7  | 54.9(3)      | C20 | C19 | C3  | C22A| 170.5(12)   |
| C4  | C5  | C6  | C9  | -178.4(2)    | C21 | C16 | C17 | C18 | -0.4(3)      |
| C5  | C6  | C7  | C8  | -56.0(3)     | C22 | C23 | C24 | C25 | 76.4(5)      |
| C5  | C6  | C9  | C10 | 106.8(2)     | C22 | C23 | C24 | C30 | -162.7(4)    |
| C5  | C6  | C9  | C14 | -72.5(3)     | C22A| C23A| C24A| C25A| -161.4(13)   |

Table 4 Torsion Angles for 14.
C6  C7  C8  C3  56.8(3)  C22A C23A C24A C30A 74.8(14)
C6  C9  C10 C11 178.6(2)  C23  C22  O3  C19  173.5(3)
C6  C9  C14 C13-178.8(2)  C23  C24  C25  C26 -159.0(3)
C7  C6  C9  C10-128.5(2)  C23A C22A O3  C19 -154.7(7)
C7  C6  C9  C14 52.2(3)  C23A C24A C25A C26  87.4(10)
C8  C3  C4  C5  54.0(3)  C24  C25  C26  C27  63.5(4)
C9  C6  C7  C8  177.90(19)  C24  C25  C26  C28  178.8(3)
C9  C10 C11 C12 0.0(3)  C24  C25  C26  C29 -61.3(4)
C10 C9  C14 C13 1.9(3)  C24A C25A C26  C27 -58.9(9)
C10 C11 C12 C13 2.3(3)  C24AC25AC26  C28  87.0(8)
C10 C11 C12 O1  178.68(19)  C24AC25AC26  C29 -167.3(8)
C11 C12 C13 C14-2.5(3)  C30  C24  C25  C26  82.5(5)
C11 C12 O1  C15 114.6(2)  C30AC24AC25AC26 -147.9(8)
C12 C13 C14 C9  0.3(3)  O1  C12  C13  C14 -178.71(19)
C13 C12 O1  C15-69.0(3)  O1  C15  C16  C17  8.2(3)
C14 C9  C10 C11-2.1(3)  O1  C15  C16  C21 -171.7(2)
C15 C16 C17 C18 179.7(2)  O2  C15  C16  C17 -171.6(2)
C15 C16 C21 C20-179.7(2)  O2  C15  C16  C21  8.5(4)
C16 C15 O1  C12-178.46(18)  O2  C15  O1  C12  1.3(3)
C16 C17 C18 C19  0.3(3)  O3  C19  C20  C21  180.0(2)
C17 C16 C21 C20  0.4(4)  O3  C22  C23  C24  72.3(5)
C17 C18 C19 C20-0.2(3)  O3  C22A C23A C24A-179.4(11)
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