

Supporting Information

Unexpected liquid crystalline behaviour of three-ring bent-core mesogens: Bis(4-subst.-phenyl) 2-methyl-*iso*-phthalates

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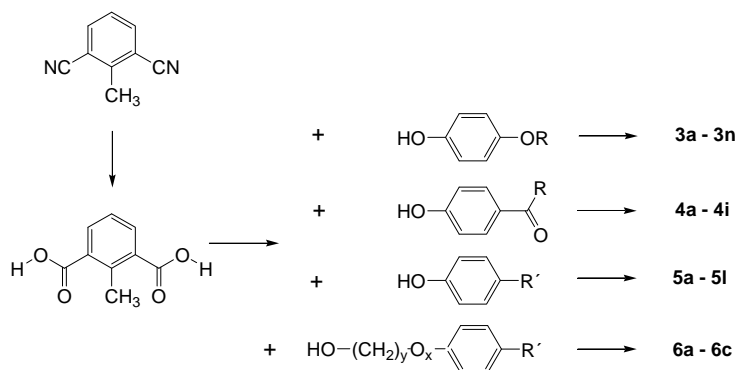
1. Synthesis and analytical data

1.1. Symmetric compounds **3a-3n**, **4a-4i**, **5a-5l**, **6a-6c**

1.2. Variation of the reaction pathway to prepare compound **5j**

1.3. Synthesis of the non-symmetric compound **2c**

1.1. Symmetric compounds **3a-3n**, **4a-4i**, **5a-5l**, **6a-6c**



Scheme S1: General scheme of the preparation of the symmetric compounds **3a-3n**, **4a-4i**, **5a-5l**, **6a-6c**

General procedure to prepare symmetric bis(4-subst.-phenyl) 2-methylisophthalates **3a-3n**, **4a-4i**, **5a-5l**, **6a-6c**

A mixture of 0.022 mol of the corresponding 4-subst.-phenol or hydroxy compound, respectively, 0.01 mol 2-methylisophthalic acid (prepared by saponification of 2,6-dicyanotoluene according to Lindsay et al. [S1]), 0.022 mol dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine in 100 ml dichloromethane was stirred at room temperature for about 24 h. Precipitated dicyclohexylurea was separated, the dichloromethane evaporated and the crude material purified by recrystallization from DMF-ethanol.

Bis(4-n-decyloxyphenyl) 2-methylisophthalate **3j**

Elemental analysis: $C_{41}H_{56}O_6$ (Mm: 644.41). C 76.36, H 8.75 (calc.); C 76.32, H 8.70 (found).

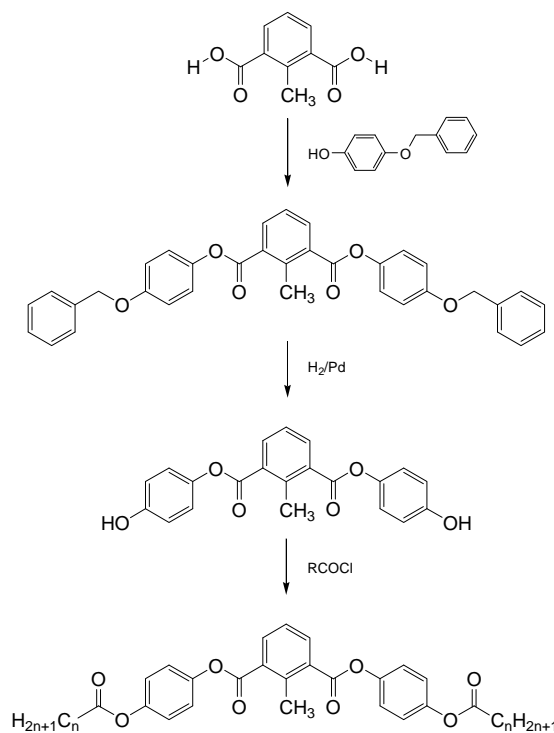
1H NMR (400 MHz, $CDCl_3$): δ 0.85-0.89 (m, 6 H, 2 x CH_3), 1.26-1.78 (m, 32 H, 16 x CH_2), 2.85 (s, 3H, Ar- CH_3), 3.92-3.96 (m, 4 H, OCH_2), 6.91-6.94 (m, 4 H, Ar-H), 7.09-7.13 (m, 4 H, Ar-H), 7.41 (t, $^3J = 8.5$ Hz, 1 H, Ar-H), 8.14 (d, $^3J = 7.9$ Hz, 2 H, Ar-H)

Bis(4-n-propionylphenyl) 2-methylisophthalate **4c**

Elemental analysis: $C_{27}H_{24}O_6$ (Mm: 444.16). C 72.96, H 5.44 (calc.); C 72.94, H 5.46 (found).

1H NMR (400 MHz, $CDCl_3$): δ 1.21-1. (m, 6 H, 2 x CH_3), 2.88 (s, 3H, Ar- CH_3), 2.98-3.03 (m, 4 H, CH_2CO), 7.31-7.34 (m, 4 H, Ar-H), 7.41 (t, $^3J = 7.8$ Hz, 1 H, Ar-H), 8.04-8.07 (m, 4 H, Ar-H), 8.21 (d, $^3J = 7.9$ Hz, 2 H, Ar-H)

1.2. Variation of the reaction pathway to prepare compound **5j**



Scheme S2: Reaction pathway to prepare compound **5j** ($n = 7$)

Bis(4-benzyloxyphenyl) 2-methylisophthalate

A mixture of 4.4 g (0.022 mol) 4-benzyloxyphenol, 1.8 g (0.01 mol) 2-methylisophthalic acid, 4.6 g (0.022 mol) dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine in 150 ml dichloromethane was stirred at room temperature for about 24 h. Precipitated dicyclohexylurea was separated, the dichloromethane evaporated and the crude material purified by recrystallization from DMF-ethanol. Yield: 4.06 g, 74.6%, mp. 165-167 °C. Elemental analysis: C₃₅H₂₈O₆ (Mm = 544.19). C 77.19, H 5.18 (calc.); C 77.20, H 5.19 (found).

¹H NMR (400 MHz, CDCl₃): δ 2.85(s, 1 H, Ar-H), 5.07 (s, 4 H, ArCH₂O), 7.00-7.03 (m, 4 H, Ar-H), 7.11-7.14 (m, 4 H, Ar-H), 7.32-7.38 (m, 10 H, Ar-H), 7.41 (t, ³J = 7.5 Hz, 1 H, Ar-H), 8.14 (d, ³J = 7.7 Hz, 2 H, Ar-H)

Bis(4-hydroxyphenyl) 2-methylisophthalate

Hydrogenation of 2.7 g (0.005 mol) bis(4-benzyloxyphenyl) 2-methylisophthalate in 100 ml ethyl acetate with 0.9 g Pd 10% on carbon resulted in 1.5 g (82.0 %) white crystals, recrystallized from DMF-ethanol. mp. 224-226 °C. Elemental analysis: C₂₁H₁₆O₆ (Mm: 364.09). C 69.23, H 4.43 (calc.); C 69.21, H 4.47 (found).

¹H NMR (400 MHz, CDCl₃): δ 2.72 (s, 3 H, Ar-CH₃), 6.75-6.78 (m, 4 H, Ar-H), 6.88-6.92 (m, 4 H, Ar-H), 7.30 (t, ³J = 7.8 Hz, 1 H, Ar-H), 8.01 (d, ³J = 7.7 Hz, 2 H, Ar-H)

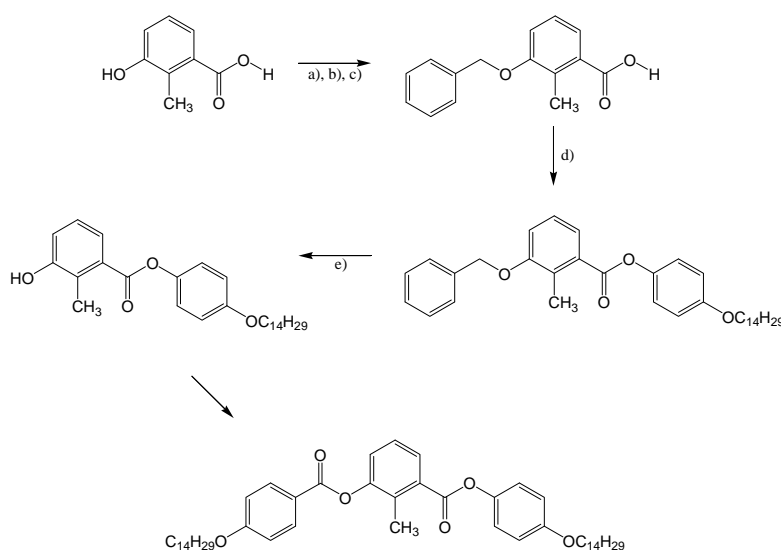
Bis(4-octanoyloxyphenyl) 2-methylisophthalate **5j**

A solution of 0.72 g (0.002 mol) bis(4-hydroxyphenyl) 2-methylisophthalate, 0.60 ml (0.005 mol) triethylamine and a catalytic amount of 4-dimethylaminopyridine in 30 ml toluene was cooled down to 10 °C. Under stirring 0.65 g (0.004 mol) octanoyl chloride was added dropwise. After stirring for 24 h at room temperature, the mixture was heated at 60 °C for further two hours. After cooling the triethylamine hydrochloride was separated and the solvent evaporated. The residue was crystallized from ethanol several times. Yield: 0.48 g (38.7 %). Melting behaviour see Table

Elemental analysis: C₃₇H₄₄O₈ (Mm 616.30), C 72.06, H 7.19 (calc.); C 72.14, H 7.24 (found)

¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, ³J = 6.5 Hz, 6 H, CH₃), 1.29-1.50 (m, 16 H, CH₂), 1.71-1.78 (m, 4 H, CH₂CH₂COO), 2.55 (t, ³J = 7.5 Hz, 4 H, CH₂COO), 2.86 (s, 3 H, Ar-CH₃), 7.12-7.26 (m, 8 H, Ar-H), 7.44 (t, ³J = 7.8 Hz, 1 H, Ar-H), 8.17 (d, ³J = 7.9 Hz, 2 H, Ar-H)

1.3. Synthesis of the non-symmetric compound **2c**



Scheme S3: Synthetic scheme for the preparation of the non-symmetric compound (**2c**): a) CH₃OH/HCl; b) benzylbromide; c) KOH d) 4-n-tetradecyloxyphenol, DCC, CH₂Cl₂; e) Pd/H₂; f) 4-n-tetradecyloxybenzoic acid, DCC, CH₂Cl₂

3-Benzyloxy-2-methylbenzoic acid

3-Hydroxy-2-methylbenzoic acid was transferred to the methyl ester with HCl gas according to Peixoto et al. [S2]. Etherification with benzylbromide and saponification of the methyl ester resulted in 3-benzyloxy-2-methylbenzoic acid [S3].

Elemental analysis: C₁₅H₁₄O₃ (Mm: 242.09). C 74.36, H 5.82 (calc.); C 74.16, H 5.80 (found). mp. 125-127 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.58 (s, 3H, Ar-CH₃), 5.10 (s, 2 H, CH₂O), 7.09 (d, ³J = 8.1 Hz, 1 H, Ar-H) 7.20 (t, ³J = 8.0 Hz, 1 H, Ar-H), 7.32-7.45 (m, 5 H, Ar-H), 7.61 (d, ³J = 7.9 Hz, 1 H, Ar-H)

4-n-Tetradecyloxyphenyl 3-benzyloxy-2-methylbenzoate:

A mixture of 1.53 g (0.005 mol) 4-tetradecyloxyphenol, 1.21 g (0.005 mol) 3-benzyloxy-2-methylbenzoic acid, 1.04 g (0.005 mol) dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine in 40 ml dichloromethane was stirred at room temperature for about 24 h. Precipitated dicyclohexylurea was separated, the dichloromethane evaporated and the crude material purified by crystallization from ethanol. Yield: 2.30 g, 86.8 %, mp. 67-68 °C. Elemental analysis: C₃₅H₄₆O₄ (Mm: 530.34). C 79.21, H 8.74 (calc.); C 79.12, H 8.71 (found). ¹H NMR (400 MHz, CDCl₃): δ 0.85-0.87 (m, 3 H, CH₃), 1.25-1.53 (m, 22 H, CH₂), 1.73-1.80 (m, 2 H, OCH₂CH₂) 2.56 (s, 3 H, Ar-CH₃), 3.94 (t, ³J = 6.6, 2 H, CH₂O) 5.11 (s, 2 H, CH₂OAr), 6.89-6.93 (m, 3H, Ar-H), 7.08-7.11 (m, 3 H, Ar-H), 7.38-7.44 (m, 5 H, Ar-H), 7.64 (d, ³J = 8.9 Hz, 1 H, Ar-H)

4-n-Tetradecyloxyphenyl 3-hydroxy-2-methylbenzoate:

Hydrogenation of 2.3 g 4-n-tetradecyloxyphenyl 3-benzyloxy-2-methylbenzoate in 100 ml ethyl acetate with 0.9 g Pd 10% on carbon resulted in 1.34 g (70.5 %) white crystals, recrystallized from ethanol. mp. 65-66 °C °C.

Elemental analysis: C₂₈H₄₀O₄ (Mm: 440.29): C 76.33, H 9.15 (calc.); C 76.34, H 9.17 (found). ¹H NMR (400 MHz, CDCl₃): δ 0.87 (t, ³J = 6.8 Hz, 3 H, CH₃), 1.25-1.33 (m, 22 H, CH₂), 1.75-1.79 (m, 2 H, CH₂CH₂O), 2.51 (s, 3 H, Ar-CH₃), 3.93 (t, ³J = 6.6 Hz, 2 H, CH₂O), 5.02 (s, 1 H, OH), 6.89-6.98 (m, 3 H, Ar-H), 7.08-7.15 (m, 3 H, Ar-H), 7.64 (d, ³J = 7.6, 1 H, Ar-H)

4-n-Tetradecyloxyphenyl 3-(4-n-tetradecyloxybenzoyloxy)-2-methylbenzoate (**2c**)

0.44 g (0.001 mol) 4-n-tetradecyloxyphenyl 3-hydroxy-2-methylbenzoate, 0.33 g (0.001 mol) 4-n-tetradecyloxybenzoic acid, 0.26 g (0.0012 mol) dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine in 20 ml dichloromethane was stirred at room temperature for about 24 h. Precipitated dicyclohexylurea was separated, the dichloromethane evaporated and the crude material purified by crystallization from ethanol. Yield: 0.43 g, 56.9 %.

Elemental analysis: C₄₉H₇₂O₆ (Mm: 756.53). C 77.74, H 9.59 (calc.); C 77.84, H 9.61 (found). ¹H NMR (400 MHz, CDCl₃): δ 0.85-0.88 (m, 6 H, CH₃), 1.25-1.53 (m, 44 H, CH₂), 1.73-1.84 (m, 4 H, CH₂CH₂O), 2.50 (s, 3 H, Ar-CH₃), 3.95 (t, ³J = 6.5 Hz, 2 H, CH₂O), 4.03 (t, ³J = 6.5 Hz, 2 H, CH₂O), 6.90-7.11 (m, 6 H, Ar-H), 7.33-7.37 (m, 2 H, Ar-H), 8.01-8.03 (m, 1 H, Ar-H), 8.15 (d, ³J = 8.9 Hz, 2 H, Ar-H)

2. Additional X-ray data

2.1. X-ray crystal structure analysis of **4b**

Table S1: Selected bond lengths (pm) and angles (°) for compound **4b** in the crystal, mean-square deviations in parentheses (atomic numbering see Fig. 2, Symmetry code i: x, 0.5 -y, z):

Atoms	Bond length
C(1)-C(2) ⁱ	138.3(2)
C(1)-C(2)	138.3(2)
C(2)-C(3)	139.6(2)
C(3)-C(4)	140.9(2)
C(3)-C(6)	149.8(2)
C(4)-C(3) ⁱ	140.9(2)
C(4)-C(5)	151.1(3)
C(6)-O(2)	119.8(2)
C(6)-O(1)	136.1(2)
C(7)-C(12)	137.8(2)
C(7)-C(8)	138.3(2)
C(7)-O(1)	141.1(2)
C(8)-C(9)	138.4(2)
C(9)-C(10)	140.1(2)
C(10)-C(11)	139.2(2)

C(10)-C(13)	150.7(2)
C(11)-C(12)	139.3(2)
C(13)-O(3)	122.2(2)
C(13)-C(14)	150.8(2)
C(14)-C(15)	151.5(2)

Atoms	Bond angle
C(2) ⁱ -C(1)-C(2)	119.7(2)
C(1)-C(2)-C(3)	120.3(2)
C(2)-C(3)-C(4)	121.4(2)
C(2)-C(3)-C(6)	117.1(1)
C(4)-C(3)-C(6)	121.34(15)
C(3) ⁱ -C(4)-C(3)	116.82(19)
C(3) ⁱ -C(4)-C(5)	121.6(1)
C(3)-C(4)-C(5)	121.6(1)
O(2)-C(6)-O(1)	123.5(1)
O(2)-C(6)-C(3)	126.64(14)
O(1)-C(6)-C(3)	109.80(13)
C(12)-C(7)-C(8)	121.98(14)
C(12)-C(7)-O(1)	115.9(1)
C(8)-C(7)-O(1)	121.8(1)
C(7)-C(8)-C(9)	118.4(1)
C(8)-C(9)-C(10)	121.4(1)
C(11)-C(10)-C(9)	118.5(1)
C(11)-C(10)-C(13)	122.1(1)
C(9)-C(10)-C(13)	119.4(1)
C(10)-C(11)-C(12)	120.7(1)
C(7)-C(12)-C(11)	119.01(14)
O(3)-C(13)-C(10)	119.74(14)
O(3)-C(13)-C(14)	121.4(1)
C(10)-C(13)-C(14)	118.9(1)
C(13)-C(14)-C(15)	113.8(2)
C(6)-O(1)-C(7)	120.5(1)

2.2. X-ray diffraction on the liquid crystalline phases:

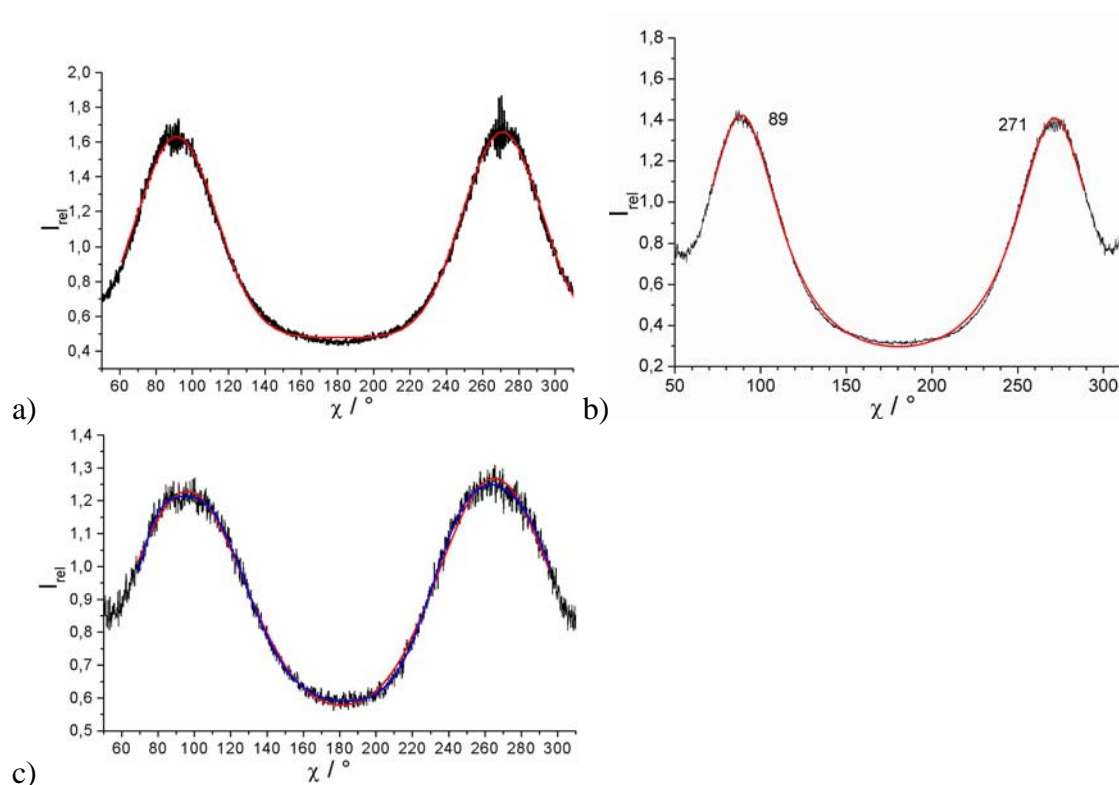


Figure S1. χ -scans for the outer diffuse scattering for the X-ray patterns on surface-aligned samples of compounds **4h** at 110 °C (a), **4i** at 115 °C (b), **5k** at 105 °C (c), all on cooling, with Gaussian fits for the relative intensity $I_{rel} = I(T)/I(\text{isotropic liquid})$ (black lines) for two maxima (red lines, in (c) for the SmC phase only for comparison) and for 4 maxima (blue line).

3. Quantum chemical studies

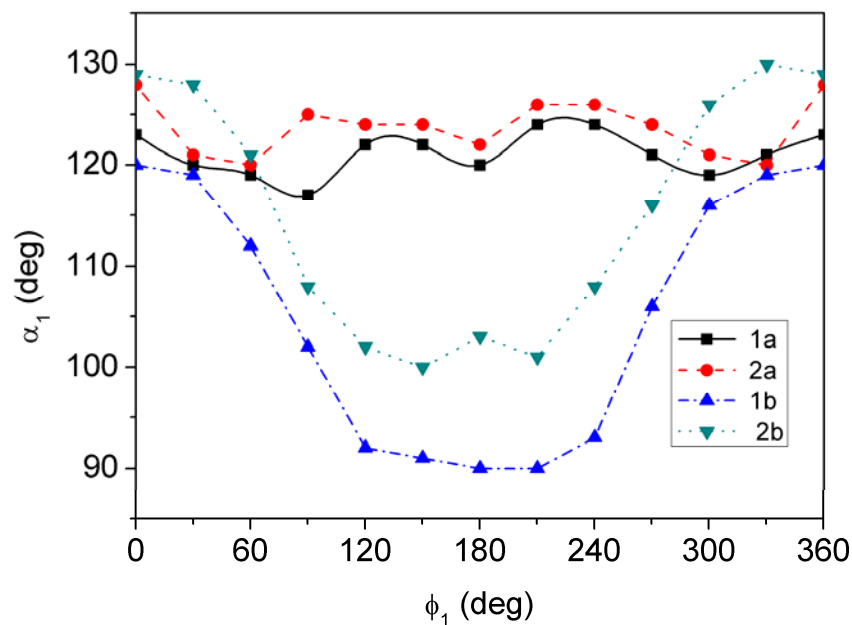


Figure S2 One-fold scans of the bending angle α_1 related to the torsion angles ϕ_1 /C-O (**1a**, **2a**) and ϕ_1 /C-C (**1b**, **2b**)

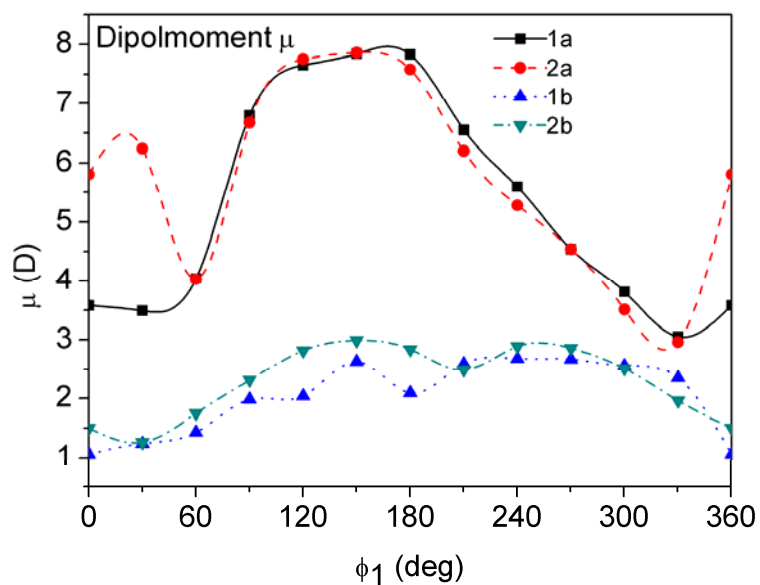


Figure S3 One-fold scans of the dipole moment μ related to the torsion angles ϕ_1 /C-O (**1a**, **2a**) and ϕ_1 /C-C (**1b**, **2b**)

References

- [S1] W. S. Lindsay, P. Stokes, L. G. Humber, V. Boekelheide, *J. Am. Chem. Soc.* 1961, 83, 943-949
- [S2] C. Peixoto, P. Laurin, M. Klinch, C. Dupuis-Hamelin, P. Mauvais, P. Lassaigne, A. Bonnefoy, B. Musicki, *Tetrahedron Lett.* 2000, 41, 1741-1745
- [S3] PLEXXIKON, INC, WO2007/2325 A1, 2007