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Supporting Information

Planar and distorted Indigo as core motif in novel chromophoric liquid crystals

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Syntheses and Analytics:

Instruments:

IR: Infrared spectra were obtained using a *Perkin-Elmer* Paragon 1000 FTIR spectrometer and are given in cm^{-1} units. All samples were measured as ATR on a ZnSe crystal. Signals are characterized by b, broad; w, weak; m, medium; s, strong.

^{1}H-NMR: The ^{1}H-NMR spectra were recorded on *Bruker* AC 300, *Bruker* DPX 300 spectrometers operating at 300 MHz or on a *Bruker* DRX 500 spectrometer operating at 500 MHz. Chemical shifts are reported as δ in ppm and the coupling constant, J,in Hz units. In all spectra solvent peaks were used as internal standard. As solvent DMSO-d6 (δ = 2.49 ppm) or $CDCl_3$ (δ = 7.24 ppm) were used. Splitting patterns are designated as follows: s, singlet; d, doublet; t,triplet; q, quartet; m, multiplet; br, broad.

^{13}C-NMR: The ^{13}C-NMR spectra were recorded either on a *Bruker* AC 300 spectrometer operating at 75 MHz or on *Bruker* DRX 500 spectrometer instrument operating at 125 MHz.

^{19}F-NMR: The ^{19}F-NMR spectra were recorded either on a *Bruker* Avance II 300 spectrometer operating at 282 MHz.

LR-MS: *Finnigan* MAT Incos 50 Galaxy System.

HR-MS: *Finnigan* MAT 900S. EI, 70eV, Peakmatching using Polyfluorocerosine.

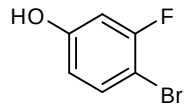
Elemental analysis: CHN-combustion analyses were measured using an Elementar Vario EL Instrument.

WAXS: Magnetic field (1.5 T) oriented samples in home made flatfilm camera, freestanding in an hole sampleholder. Temperature controller from *Lakeshore*. Two dimensional diffraction patterns detected on *Fuji* BAS SR 3000 imaging plates and processed with the X-Ray 1.0 software from the Université Mons Hainaut.

Single Crystal X-Ray: The single crystal X-ray analysis for compound **12** was done on a Kappa CCD four-circle diffractometer from *Nonius* with a Mo X-ray source. Compound **23** was measured on an *Agilent* Super-Nova with a Cu X-ray source. The structures were resolved and refined using the SHELX-97 software package. Visual representation, the introduction of dummy atoms and lines as well as the determination of distances and angles was performed using the Diamond 3.0 software of *Crystal Impact*.

Syntheses of the Boronic Acids:

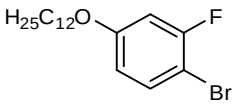
4-Bromo-3-fluorophenol (26)



26

80 mmol (9.00 g) of 3-fluorophenol have been converted with 81 mmol (12.96 g) bromine according to literature.[1] After recrystallisation from petrolether (40-60 °C) 4.01 g (19%) **26** have been yielded as colourless solid. R_f=0.38 (SiO_2, *c*Hex/EtOAc 3:1); m.p. Cr 71°C I (PE); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.34 (m, 1H; 5-H), 6.64 (dd, $^3J_{H,F}$=9.7 Hz, ^4J=2.8 Hz, 1H; 2-H), 6.52 (ddd, ^3J=8.7 Hz, ^4J=2.8 Hz, $^5J_{H,F}$=1.0 Hz, 1H; 6-H), 5.21 ppm (s, 1H; OH); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=159.38 (s, $^1J_{C,F}$=246.8 Hz; C-3), 155.92 (s, $^3J_{C,F}$=10.2 Hz; C-1), 133.59 (d; C-5), 112.63 (d, $^4J_{C,F}$=2.9 Hz; C-6), 104.51 (d, $^2J_{C,F}$=25.2 Hz; C-2), 99.59 ppm (s, $^2J_{C,F}$=21.1 Hz; C-4); ^{19}F NMR (282.2 MHz, $CDCl_3$, 25°C): δ=-105.04 ppm (m; 3-F); IR (ATR): $\tilde{\nu}$=3334 (bw), 1595 (s), 1484 (s), 1442 (s), 1296 (s), 1238 (m), 1215 (m), 1148 (s), 1123 (s), 1042 (m), 961 (s), 839 (m), 799 (m), 735 (m), 607 cm^{-1} (s); MS (EI, 70 eV) m/z (%): 192 (100) [M^+ for ^{81}Br], 190 (100) [M^+ for ^{79}Br], 111 (17) [M^+-Br], 83 (80), 57 (28).

1-Bromo-2-fluoro-4-dodecyloxybenzene (27)

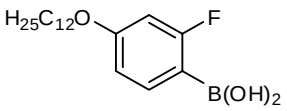


27

16 mmol (3.07 g) 4-bromo-3-fluorophenol (**26**), 17 mmol bromododecane (4.00 g) and 20 mmol (0.80 g) NaOH have been dissolved in 15 ml DMSO and heated to 100 °C for 12 hours. After cooling to room temperature the solution has been extracted with MTBE and washed three times with water and dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product was purified chromatographically (silica gel, *c*hex) yielding 5.57 g (97%) **27** as colourless oil. R_f=0.75 (SiO_2, *c*Hex/EtOAc 3:1); n_D^{20} 1.5013; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.36 (m, 1H; 6-H), 6.66 (dd, $^3J_{H,F}$=10.5 Hz, ^4J=2.8 Hz, 1H; 3-H), 6.57 (ddd, ^3J=8.8 Hz, ^4J=2.8 Hz, $^5J_{H,F}$=0.9 Hz, 1H; 6-H), 3.89 (t ^3J=6.5 Hz, 2H; α-CH_2); 1.75 (m, 2H; β-CH_2), 1.48-1.18 (m, 18H; CH_2), 0.87 ppm (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=159.75 (s, $^3J_{C,F}$=9.8 Hz; C-4), 159.43 (s, $^1J_{C,F}$=246.0 Hz; C-2), 133.19 (d; C-6), 111.82 (d, $^4J_{C,F}$=2.5 Hz; C-5), 103.25 (d, $^2J_{C,F}$=25.4 Hz; C-3), 98.88 (s, $^2J_{C,F}$=21.2 Hz; C-1), 68.60 (t; α-CH_2), 31.91, 29.63, 29.57, 29.34 (4 × t; CH_2), 29.01 (t; β-CH_2), 25.93 (t; γ-

CH_2), 22.68 (t; CH_2), 14.10 ppm (q; CH_3); ^{19}F NMR (282.2 MHz, $CDCl_3$, 25°C): δ=-105.50 ppm (m; 2-F); IR (ATR): $\tilde{\nu}$=2920 (s), 2850 (s), 1603 (m), 1582 (m), 1487 (s), 1465 (m), 1320 (m), 1290 (m), 1260 (m), 1165 (s), 1143 (m), 1051 (w), 1016 (w), 830 (m), 790 (w), 718 (w), 641 cm^{-1} (w); MS (EI, 70 eV) m/z (%): 360 (15) [M^+ for ^{81}Br], 358 (16) [M^+ for ^{79}Br], 280 (4) [M^+-Br], 192 (100) [M^+-$C_{12}H_{25}$ for ^{81}Br], 190 (100) [M^+-$C_{12}H_{25}$ for ^{79}Br], 112 (19), 97 (7), 83 (16), 69 (19), 57 (37), 43 (39).

2-Fluoro-4-dodecyloxyphenyl boronic acid (6)

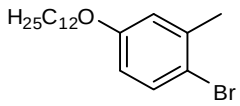


6

7.7 mmol (2.79 g) of 1-bromo-2-fluoro-4-dodecyloxybenzene (**27**) were dissolved in 35 ml dry THF and cooled to -78 °C. 7.8 mmol (3.1 ml) of a 2.5 molar *n*BuLi solution were added slowly over 90 minutes. 30 minutes after complete addition 21.0 mmol (2.0 ml) trimethylborate were added rapidly and the solution was allowed to reach room temperature. Subsequently 50 ml 2 molar HCl were added and THF was removed under reduced pressure. After addition of ethyl acetate the organic phase was washed twice with water and once with brine and dried over $MgSO_4$. The solvent was evaporated and crude product recrystallized from petrolether (40-60 °C) yielding 1.67 g (63%) 2-fluoro-4-dodecyloxyphenyl boronic acid (**6**) as colourless solid. R_f=0.25 (SiO_2, *c*Hex/EtOAc 3:1); m.p. Cr 92 °C I (PE); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.70 (m, 1H; 6-H), 6.71 (dd, ^3J=8.4 Hz, ^4J=2.2 Hz, 1H; 5-H), 6.53 (dd, $^3J_{H,F}$=13.0 Hz, ^4J=2.1 Hz, 1H; 3-H), 3.95 (t ^3J=6.5 Hz, 2H; α-CH_2); 1.77 (m, 2H; β-CH_2), 1.48-1.18 (m, 18H; CH_2), 0.86 ppm (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=169.04 (s, $^1J_{C,F}$=255.1 Hz; C-2), 163.43 (s; C-4), 137.47 (d, $^3J_{C,F}$=9.7 Hz; C-6), 111.02 (d; C-5), 101.31 (d, $^2J_{C,F}$=29.5 Hz; C-3), 68.38 (t; α-CH_2), 31.92, 29.64, 29.58, 29.34 (4 × t; CH_2), 29.03 (t; β-CH_2), 25.95 (t; γ-CH_2), 22.69 (t; CH_2), 14.12 ppm (q; CH_3);[i] ^{19}F NMR (282.2, $CDCl_3$, 25°C): δ=-107.56 ppm (m; 2-F); IR (ATR): $\tilde{\nu}$=3508 (bw), 3351 (bw), 3208 (bw), 2917 (s), 2850 (m), 1621 (s), 1565 (m), 1469 (m), 1429 (m), 1381 (m), 1345 (s), 1289 (m), 1232 (w), 1194 (w), 1147 (m), 1114 (s), 1027 (m), 1004 (m), 956 (w), 933 (w), 837 (m), 784 (m), 725 (m), 647 cm^{-1} (m).

[i] The signal for the quarternary C-1 could not be found for **6**.

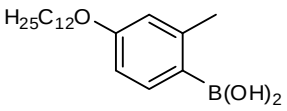
1-Bromo-4-dodecyloxy-2-methylbenzene (28)



28

50 mmol (9.35 g) m-bromocresole, 52 mmol bromododecane (12.2 g) and 60 mmol (2.4 g) NaOH have been dissolved in 50 ml DMSO and heated to 100 °C for 12 hours. After cooling to room temperature the solution has been extracted with MTBE and washed three times with water and dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product was purified chromatographically (silica gel, *c*hex) yielding 14.55 g (82%) **28** as colourless oil. R_f=0.66 (SiO_2, *c*Hex/EtOAc 5:1); n_D^{22} : 1.5132; ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=7.36 (d, ^3J=8.7 Hz, 1H; 6-H), 6.77 (d, ^4J=2.9 Hz, 1H; 3-H), 6.59 (dd, ^3J=8.7 Hz, ^4J=3.0 Hz, 1H; 5-H), 3.89 (t, ^3J=6.5 Hz, 2H; α-CH_2), 2.35 (s, 3H; 2-CH_3), 1.75 (m, 2H; β-CH_2), 1.42 (m, 2H; γ-CH_2), 1.30-1.20 ppm (m, 16H; CH_2), 0.88 (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=158.34 (s; C-4), 138.65 (s; C-2), 132.70 (d; C-6), 117.10 (d; C-3), 115.11 (s; C-1), 113.44 (d; C-5), 68.14 (t; α-CH_2), 31.91, 29.65, 29.38, 29.35 (4 × t; CH_2), 29.22 (t; β-CH_2), 26.01 (t; γ-CH_2), 23.09 (q; C-3-*C*H_3), 22.69 (t; CH_2), 14.11 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=2919 (s), 2850 (s), 1588 (w), 1571 (m), 1466 (s), 1377 (m), 1306 (s), 1288 (s), 1237 (s), 1170 (s), 1142 (m), 1126 (m), 1051 (m), 1022 (s), 861 (m), 840 (m), 794 (m), 720 (w), 962 (w), 636 cm^{-1} (m); MS (EI, 70 eV) m/z (%): 356 (39) [M^+ for ^{81}Br], 354 (40) [M^+ for ^{79}Br], 276 (36) [M^+-Br], 188 (100) [M^+-$C_{12}H_{25}$ for ^{81}Br], 186 (100) [M^+-$C_{12}H_{25}$ for ^{79}Br], 108 (14) [M^+-$C_{12}H_{25}$ -Br]; elemental analysis calcd (%) for $C_{19}H_{31}BrO$: C 64.22, H 8.79, found: C 64.60, H 8.87.

4-Dodeclyloxy-2-methylphenyl boronic acid (7)



7

40 mmol (14.2 g) 1-bromo-4-dodecyloxy-2-methylbenzene (**28**) were dissolved in 200 ml dry THF and cooled to -78 °C. 42 mmol (16.8 ml) of a 2.5 molar *n*BuLi solution were added slowly over 90 minutes. 30 minutes after complete addition 120.0 mmol (11.4 ml) trimethylborate were added rapidly and the solution was allowed to reach room temperature. Subsequently 100 ml 2 molar HCl were added and THF was removed under reduced pressure. After addition of ethyl acetate the organic phase was washed twice with water and once with brine and dried over $MgSO_4$. The solvent was evaporated and crude product recrystallized from petrolether (40-60 °C) yielding 11.38 g (89%) 4-dodeclyloxy-2-methylphenyl boronic

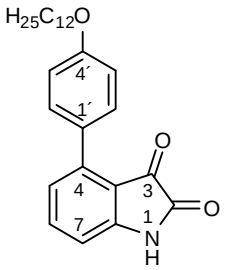
acid (**7**) as colourless solid. R_f=0.61 (SiO_2, EtOAc); m.p. Cr 67 °C I (PE); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.13 (d, ^3J=8.1 Hz, 1H; 6-H), 6.78 (m, 2H; 3-H and 5-H), 3.89 (t, ^3J=4.0 Hz, 2H; α-CH_2), 2.77 (s, 3H; 2-CH_3), 1.78 (m, 2H; β-CH_2), 1.41 (m, 2H; γ-CH_2), 1.30-1.20 (m, 16H; CH_2), 0.89 ppm (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=162.17 (s; C-4), 148.51 (s; C-2), 139.30 (d; C-6), 116.77 (d; C-3), 110.85 (d, C-5), 67.71 (t; α-CH_2), 31.93, 29.62, 29.42, 29.37 (4 × t; CH_2), 29.26 (t; β-CH_2), 26.05 (t; γ-CH_2), 23.35 (q; C-3-*C*H_3), 22.70 (t; CH_2), 14.12 ppm (q; CH_3);[ii] IR (ATR): $\tilde{\nu}$=3744 (w), 2917 (s), 2859 (s), 1600 (s), 1558 (m), 1469 (m), 1418 (m), 1341 (s), 1282 (s), 1236 (s), 1174 (m), 1126 (m), 1034 (m), 810 (m), 688 (m), 613 cm^{-1} (m).

Syntheses of the Isatin Derivatives (Type II):

General procedure A:

To a 0.12 molar solution of the respective regioisomer of bromoisatin in dry DME 1.1-1.2 eq. of the boronic acid and 2 mol% tetrakistriphenylphosphin palladium(0) were added and the slurry was heated to 90 °C under argon atmosphere. After complete solvation 2 eq. of a degassed aqueous 1 molar potassium phosphate solution was added and the solution was stirred for 7 hours before it was given on a 0.5 molar hydrochloric acid/ice mixture. After 12 hours the product was obtained as dark red precipitate, filtered, dried and purified chromatographically (silica gel, DCM/MTBE 15:1).

4-(4-(Dodecyloxy)phenyl)indolin-2,3-dione (29)



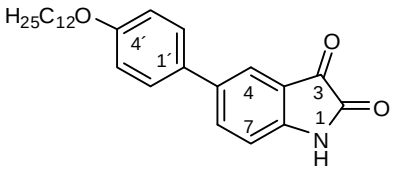
29

4.0 mmol (0.904 g) 4-bromoisatin and 4.6 mmol (1.408 g) of the boronic acid **5** have been converted and purified according to general procedure A yielding 0.383 g (24%) **29** as a orange solid. R_f=0.29 (SiO_2, DCM/MTBE 15:1); m.p. Cr 170.8 °C (28.7 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, DMSO, 25°C): δ=11.09 (s, 1H; 1-H), 7.56 (t, ^3J=7.9 Hz, 1H; 6-H), 7.49 (d, ^3J=8.7 Hz, 2H; 2´-H and 6´-H), 6.98 (d, ^3J=7.0 Hz, 1H; 5-H), 6.97 (d, ^3J=8.9 Hz, 2H; 3´-H and 5´-

[ii] The signal for the quarternary C-1 could not be found for **7**.

H), 6.82 (d, ^3J=7.8 Hz, 1H; 7-H), 4.01 (t, ^3J=6.4 Hz, 2H; α-CH_2), 1.77-1.68 (m, 2H; β-CH_2), 1.49-1.39 (m, 2H; γ-CH_2), 1.25 (s, 16H; CH_2), 0.85 ppm (t, ^3J=6.5 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, DMSO, 25°C): δ=182.87 (s; C-3), 159.16 (s; C-4′), 158.98 (s; C-2), 151.36 (s; C-7a), 141.42 (s; C-4), 137.67 (d; C-6), 130.19 (d; C-2′ and C-6′), 128.24 (s; C-1′), 123.98 (d; C-5), 113.81 (two signals: s; C-3a; d; C-3′ and C-5′), 110.28 (d; C-7), 67.41 (t; α-CH_2), 31.21, 28.93, 28.81, 28.69, 28.63, 28.59 (6 × t; CH_2), 25.44 (t; γ-CH_2), 22.01 (t; CH_2), 13.85 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=3209 (bw), 2916 (m), 2849 (m), 1720 (s), 1613 (s), 1584 (s), 1568 (m), 1514 (w), 1485 (w), 1469 (w), 1296 (w), 1249 (m), 1181 (w), 1102 (w), 910 (w), 797 (w), 729 (w), 628 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 247 (s), 368 nm (w); MS (EI, 70 eV) m/z (%): 407 (29) [M^+], 239 (54) [M^+-$C_{12}H_{25}$], 211 (100) [M^+-$C_{12}H_{25}$, -CO], 184 (10) [M^+-$C_{12}H_{25}$, -2CO], 168 (7), 154 (4), 139 (7), 127 (6), 83 (6), 69 (14), 57 (21), 55 (29); HRMS (EI, 70 eV): calcd for $C_{26}H_{33}NO_3$ [M^+]: 407.2461, found: 407.246; elemental analysis calcd (%) for $C_{26}H_{33}NO_3$: C 76.62, H 8.16, N 3.44, found: C 76.25, H 8.23, N 3.29.

5-(4-Dodecyloxyphenyl)indolin-2,3-dione (30)

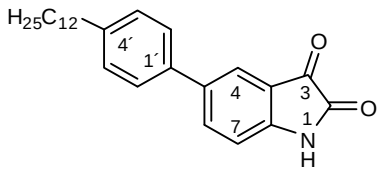


30

2.0 mmol (0.452 g) 5-bromoisatin and 2.4 mmol (0.735 g) of the boronic acid **5** have been converted and purified according to general procedure A yielding 0.556 g (68%) **30** as a orange solid. R_f=0.32 (SiO_2, DCM/MTBE 15:1); m.p. Cr 104.9 (8.1) SC 162.7 (17.0) SmA 173.7 °C (1.1 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, DMSO, 25°C): δ=11.00 (s, 1H; NH), 7.83 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 1H; 6-H), 7.68 (d, ^4J=1.7 Hz, 1H; 4-H), 7.55 (d, ^3J=8.7 Hz, 2H; 2′-H and 6′-H), 6.99 (d, ^3J=8.8 Hz, 2H; 3′-H and 5′-H), 6.98 (d, ^3J=8.0 Hz, 1H; 7-H), 4.00 (t, ^3J=6.5 Hz, 2H; α-CH_2), 1.77-1.67 (m, 2H; β-CH_2), 1.45-1.20 (m, 18H; CH_2), 0.85 ppm (t, ^3J=6.5 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, DMSO, 25°C): δ=184.03 (s; C-3), 159.15 (s; C-2), 158.13 (s; C-4′), 149.09 (s; C-7a), 135.66 (d; C-6), 134.59 (s; C-5), 130.72 (s; C-1′), 127.00 (d; C-2′ and C-6′), 121.54 (d; C-4), 118.02 (s; C-3a), 114.72 (d; C-3′ and C-5′), 112.33 (d; C-7), 67.36 (t; α-CH_2), 30.93, 28.61, 28.38 (3 × t; CH_2), 28.31 (t; β-CH_2), 25.15 (t; γ-CH_2), 21.70 (t; CH_2), 13.51 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=3206 (bm), 2914 (s), 2848 (s), 1751 (s), 1717 (s), 1627 (s), 1573 (w), 1521 (w), 1473 (s), 1394 (w), 1308 (m), 1259 (s), 1214 (s), 1185 (m), 1127 (w), 1115 (w), 1035 (w), 969 (w), 894 (w), 821 (m), 755 (w), 718 (m), 660 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 270 (s), 457 nm (w); MS (EI, 70 eV) m/z (%): 407 (41) [M^+],

379 (13) [M^+-CO], 239 (28) [M^+-$C_{12}H_{25}$], 211 (100) [M^+-$C_{12}H_{25}$, -CO], 183 (39) [M^+-$C_{12}H_{25}$, -2CO], 154 (7), 139 (7), 127 (9), 97 (3), 83 (8), 69 (18), 57 (28), 55 (34); HRMS (EI, 70 eV): calcd for $C_{26}H_{33}N\ O_3$ [M^+]: 407.2461, found: 407.246; elemental analysis calcd (%) for $C_{26}H_{33}NO_3$: C 76.62, H 8.16, N 3.44, found: C 76.64, H 8.32, N 3.33.

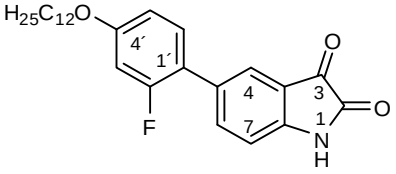
5-(4-Dodecylphenyl)indolin-2,3-dione (31)



31

4.0 mmol (0.904 g) 5-bromoisatin and 4.2 mmol (1.219 g) of the boronic acid **4** have been converted and purified according to general procedure A yielding 0.527 g (34%) **31** as a orange solid. R_f=0.26 (SiO_2, DCM/MTBE 15:1); m.p. Cr 159.6 °C (21.0 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.41 (s, 1H; NH), 7.81 (s, 1H; 4-H), 7.77 (dd, ^3J=8.2 Hz, ^4J=1.8 Hz, 1H; 6-H), 7.42 (d, ^3J=8.1 Hz, 2H; 2´-H and 6´-H), 7.24 (d, ^3J=7.9 Hz, 2H; 3´-H and 5´-H), 6.99 (d, ^3J=8.1 Hz, 1H; 7-H), 2.62 (t, ^3J=7.6 Hz, 2H; α-CH_2), 1.61 (m, 2H; β-CH_2), 1.35 - 1.21 (m, 18H; CH_2), 0.86 ppm (t, ^3J=6.5 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=183.07 (s; C-3), 159.46 (s; C-2), 147.81 (s; C-7a), 142.96 (s; C-4´), 137.65 (s; C-5), 137.03 (d; C-6), 136.18 (s; C-1´), 129.11 (d; C-3´ and C-5´), 126.38 (d; C-2´ and C-6´), 123.99 (d; C-4), 118.51 (s; C-3a), 112.61 (d; C-7), 35.57 (t; α-CH_2), 31.91, 31.44, 29.65, 29.58, 29.50, 29.33, 22.68 (7 × t; CH_2), 14.12 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=3200 (bm), 2914 (s), 2847 (m), 1750 (s), 1720 (s), 1616 (m), 1478 (m), 1307 (m), 1260 (w), 1200 (w), 1120 (w), 1013 (w), 963 (w), 838 (m), 813 (w), 746 (w), 717 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 212 (m), 263 (s), 448 nm (w); MS (EI, 70 eV) m/z (%): 391 (82) [M^+], 363 (100) [M^+-CO], 335 (4), 236 (18) [M^+ -$C_{11}H_{23}$], 222 (8), 208 (73) [M^+-CO -$C_{11}H_{23}$], 193 (6), 180 (53) [M^+-2CO -$C_{11}H_{23}$], 165 (12), 152 (18), 139 (5), 127 (3), 115 (5), 57 (7); HRMS (EI, 70 eV): calcd for $C_{26}H_{33}NO_2$ [M^+]: 391.251, found: 391.251; elemental analysis calcd (%) for $C_{26}H_{33}NO_2$: C 79.76, H 8.50, N 3.58, found: C 79.76, H 8.60, N 3.46.

5-(2-Fluoro-4-(dodecyloxy)phenyl)indolin-2,3-dione (32)

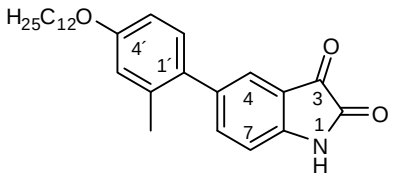


32

3.0 mmol (0.678 g) 5-bromoisatin and 3.3 mmol (1.070 g) of the boronic acid **6** have been converted and purified according to general procedure A yielding 0.904 g (71%)

32 as a red solid. R_f=0.27 (SiO_2, DCM/MTBE 15:1); m.p. Cr 92.8 (31.7) Cr_2 150.6 °C (26.2 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, DMSO, 25°C): δ=11.21 (s, 1H; NH), 7.70 (d, ^3J=8.2 Hz, 1H; 6-H), 7.56 (s, 1H; 4-H), 7.42 (m, 1H; 6′-H), 7.01 (d, ^3J=8.2 Hz, 1H; 7-H), 6.90 (dd, $^3J_{H,F}$=13.2 Hz, ^4J=2.3 Hz, 1H; 3′-H), 6.84 (dd, ^3J=8.6 Hz, ^4J=2.3 Hz, 1H; 5′-H), 4.00 (t, ^3J=6.4 Hz, 2H; α-CH_2), 1.70 (m, 2H; β-CH_2), 1.40 (m, 2H; γ-CH_2), 1.35-1.18 (m, 16H; CH_2), 0.84 ppm (t, ^3J=6.5 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, DMSO, 25°C): δ=184.17 (s; C-3), 159.46 (s, $^1J_{C,F}$=245.2 Hz; C-2′), 159.46 (s, $^3J_{C,F}$=11.5 Hz; C-4′), 159.35 (s; C-2), 149.62 (s; C-7a), 138.07 (d; C-6), 130.54 (d, $^3J_{C,F}$=4.7 Hz; C-6′), 129.45 (s; C-5), 124.08 (d; C-4), 118.68 (s, $^2J_{C,F}$=12.9 Hz; C-1′), 117.95 (s; C-3a), 112.34 (d; C-7), 111.31 (d; C-5′), 102.35 (s, $^2J_{C,F}$=26.3 Hz; C-3′), 67.95 (t; α-CH_2), 31.20, 28.89, 28.62 (3 × t; CH_2), 28.40 (t; β-CH_2), 25.32 (t; γ-CH_2), 22.00 (t; CH_2), 13.84 ppm (q; CH_3); ^{19}F NMR (282.2 MHz, DMSO, 25°C): δ=-116.19 ppm (m; 2′-F); IR (ATR): $\tilde{\nu}$=3221 (bw), 2915 (s), 2846 (m), 1772 (m), 1724 (s), 1622 (s), 1575 (w), 1479 (m), 1395 (w), 1292 (m), 1156 (m), 1129 (m), 1034 (w), 899 (w), 843 (m), 830 (m), 746 (w), 713 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 268 (s), 455 nm (w); MS (EI, 70 eV) m/z (%): 425 (39) [M^+], 397 (27) [M^+-CO], 257 (21) [M^+-$C_{12}H_{25}$], 229 (100) [M^+-$C_{12}H_{25}$ -CO], 201 (37) [M^+-$C_{12}H_{25}$ -2CO]; HRMS (EI, 70 eV): calcd for $C_{26}H_{32}FNO_3$ [M^+]: 425.2366, found: 425.236; elemental analysis calcd (%) for $C_{26}H_{32}FNO_3$: C 73.38, H 7.58, N 3.29, found: C 73.11, H 7.75, N 3.44.

5-(4-(Dodecyloxy)-2-methylphenyl)indolin-2,3-dione (33)

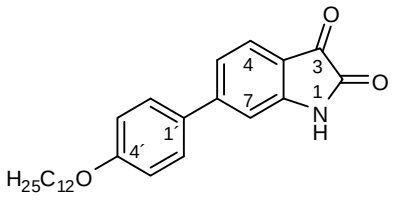


33

5.0 mmol (1.130 g) 5-bromoisatin and 5.5 mmol (1.953 g) of the boronic acid **7** have been converted and purified according to general procedure A yielding 1.201 g (57%) **33** as a orange solid. R_f=0.30 (SiO_2, DCM/MTBE 15:1); m.p. Cr 120.4 (8.0) Cr_2 158.8 °C (22.5 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=9.06 (s, 1H; NH), 7.52 (s, 1H; 4-H), 7.48 (d, ^3J=8.1 Hz, 1H; 6-H), 7.06 (d, ^3J=8.3 Hz, 1H; 6′-H), 7.02 (d, ^3J=8.0 Hz, 1H; 7-H), 6.79 (s, 1H; 3′-H), 6.76 (d, ^3J=8.4 Hz, 1H; 5′-H), 3.96 (t, ^3J=6.5 Hz, 2H; α-CH_2), 2.22 (s, 3H; 2′-CH_3), 1.78 (m, 2H; β-CH_2), 1.50-1.10 (m, 18H; CH_2), 0.86 ppm (t, ^3J=6.4 Hz, 3H; alkyl-CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=183.46 (s; C-3), 159.96 (s; C-2), 158.78 (s; C-4′), 147.82 (s; C-7a), 139.68 (d; C-6), 137.93 (s; C-5), 136.51 (s; C-2′), 131.89 (s; C-1′), 130.52 (d; C-6′), 126.31 (d; C-4), 117.83 (s; C-3a), 116.56 (d; C-3′), 112.34 (d; C-7), 111.95 (d; C-5′), 67.99 (t; α-CH_2), 31.89, 29.58, 29.37, 29.33 (4 × t; CH_2), 29.27 (t; β-CH_2), 26.03 (t; γ-CH_2), 22.67 (t; CH_2), 20.64 (q; C-2′-CH_3), 14.10 ppm (q;

alkyl-CH_3); IR (ATR): $\tilde{\nu}$=3288 (bw), 2915 (s), 2849 (m), 1759 (m), 1739 (s), 1711 (s), 1617 (s), 1568 (w), 1472 (s), 1394 (w), 1364 (w), 1289 (m), 1232 (m), 1197 (m), 1170 (m), 1120 (m), 1052 (w), 964 (w), 905 (w), 861 (w), 851 (m), 789 (w), 750 (w), 716 (w), 650 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 215 (m), 255 (s), 437 nm (w); MS (EI, 70 eV) m/z (%): 421 (27) [M^+], 393 (7) [M^+-CO], 253 (23) [M^+-$C_{12}H_{25}$], 225 (100) [M^+-CO -$C_{12}H_{25}$], 196 (12) [M^+-2CO -$C_{12}H_{25}$], 180 (5), 170 (11), 141 (6), 115 (6), 55 (10); HRMS (EI, 70 eV): calcd for $C_{27}H_{35}NO_3$ [M^+]: 421.2617, found: 421.261; elemental analysis calcd (%) for $C_{27}H_{35}NO_3$: C 76.92, H 8.37, N 3.32, found: C 76.79, H 8.41, N 3.22.

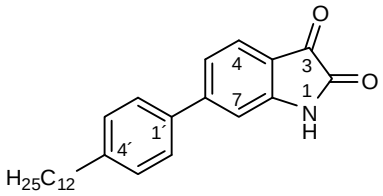
6-(4-(Dodecyloxy)phenyl)indolin-2,3-dione (34)



34

3.0 mmol (0.678 g) 6-bromoisatin and 3.5 mmol (1.058 g) of the boronic acid **5** have been converted and purified according to general procedure A yielding 1.041 g (85%) **34** as a orange solid. R_f=0.42 (SiO_2, DCM/MTBE 15:1); m.p. Cr 156.0 °C (23.9 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, DMSO, 25°C): δ=11.09 (s; 1H, 1-H), 7.66 (d, ^3J=8.8 Hz, 2H; 2´-H and 6´-H), 7.54 (d, ^3J=7.9 Hz, 1H; 4-H), 7.32 (dd, ^3J=7.9 Hz, ^4J=1.3 Hz, 1H; 5-H), 7.06 (s, 1H; 7-H), 7.05 (d, ^3J=8.8 Hz, 2H; 3´-H and 5´-H), 4.02 (t, ^3J=6.4 Hz, 2H; α-CH_2), 1.76-1.67 (m, 2H; β-CH_2), 1.47-1.37 (m, 2H; γ-CH_2), 1.24 (s, 16H; CH_2), 0.84 ppm (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, DMSO, 25°C): δ=183.56 (s; C-3), 159.85 (s; C-2), 159.63 (s; C-4´), 151.39 (s; C-7a), 149.52 (s; C-6), 130.71 (s; C-1´), 128.31 (d; C-2´ and C-6´), 125.26 (d; C-4), 120.45 (d; C-5), 116.03 (s; C-3a), 114.98 (d; C-3´ and C-5´), 109.13 (d; C-7), 67.53 (t; α-CH_2), 31.21, 28.90, 28.63 (3 × t; CH_2), 28.51 (t; β-CH_2), 25.38 (t; γ-CH_2), 22.01 (t; CH_2), 13.86 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=3275 (bm), 2914 (s), 2850 (m), 1764 (s), 1729 (s), 1715 (s), 1620 (s), 1516 (w), 1470 (m), 1446 (m), 1413 (w), 1337 (m), 1292 (w), 1244 (m), 1174 (s), 1105 (m), 1043 (w), 1021 (w), 953 (w), 893 (w), 824 (m), 796 (m), 787 (w), 730 (w), 653 (m), 626 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 220 (s), 253 (s), 358 nm (m); MS (EI, 70 eV) m/z (%): 407 (29) [M^+], 239 (34) [M^+-$C_{12}H_{25}$], 211 (100) [M^+-$C_{12}H_{25}$, -CO], 184 (14) [M^+-$C_{12}H_{25}$, -2CO], 168 (3), 155 (5), 139 (5), 127 (4), 83 (7), 69 (16), 57 (28), 55 (32); HRMS (EI, 70 eV): calcd for $C_{26}H_{33}NO_3$ [M^+]: 407.2461, found: 407.246; elemental analysis calcd (%) for $C_{26}H_{33}NO_3$: C 76.62, H 8.16, N 3.44, found: C 76.17, H 8.17, N 3.27.

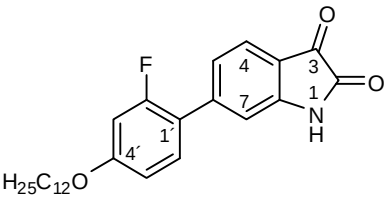
6-(4-Dodecylphenyl)indolin-2,3-dione (35)



35

4.0 mmol (0.904 g) 6-bromoisatin and 4.5 mmol (1.306 g) of the boronic acid **4** have been converted and purified according to general procedure A yielding 0.798 g (51%) **35** as a orange solid. R_f=0.35 (SiO_2, DCM/MTBE=15:1); m.p. Cr 137 °C I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.62 (s; 1H, 1-H), 7.64 (d, ^3J=7.9 Hz, 1H; 4-H), 7.52 (d, ^3J=8.0 Hz, 2H; 2′-H and 6′-H), 7.31 (d, ^3J=9.7 Hz, 1H; 5-H), 7.28 (d, ^3J=8.3 Hz, 2H; 3′-H and 5′-H), 7.14 (s, 1H; 7-H), 2.64 (t, ^3J=7.6 Hz, 2H; α-CH_2), 1.63 (m, 2H; β-CH_2), 1.38-1.18 (m, 18H; CH_2), 0.86 ppm (t, ^3J=6.5 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=182.16 (s; C-3), 160.14 (s; C-2), 151.96 (s; C-7a), 149.75 (s; C-6), 144.80 (s; C-4′), 136.39 (s; C-1′), 129.23 (d; C-3′ and C-5′), 127.11 (d; C-2′ and C-6′), 126.22 (d; C-4), 122.56 (d; C-5), 116.62 (s; C-3a), 110.61 (d; C-7), 35.70 (t; α-CH_2), 31.91, 31.34, 29.65, 29.58, 29.49, 29.34, 22.68 (7 × t; CH_2), 14.12 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=3210 (bw), 2915 (m), 2848 (m), 1748 (m), 1730 (s), 1622 (s), 1470 (w), 1444 (w), 1409 (w), 1340 (w), 1269 (w), 1176 (w), 1109 (w), 947 (w), 837 (w), 812 (w), 798 (w), 783 (w), 729 (m), 667 (w), 625 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 217 (s), 251 (s), 339 nm (m); MS (EI, 70 eV) m/z (%): 391 (37) [M^+], 363 (38) [M^+-CO], 348 (5), 334 (8), 320 (9), 306 (11), 292 (8), 278 (8), 264 (9), 250 (6), 236 (45) [M^+ -$C_{11}H_{23}$], 222 (100) [M^+ -$C_{12}H_{25}$], 209 (77) [M^+-CO -$C_{11}H_{23}$], 195 (12), 181 (93) [M^+-2CO -$C_{11}H_{23}$], 165 (18), 152 (32), 139 (7), 127 (6), 115 (9), 57 (17); HRMS (EI, 70 eV): calcd for $C_{26}H_{33}NO_2$ [M^+]: 391.2511, found: 391.251; elemental analysis calcd (%) for $C_{26}H_{33}NO_2$: C 79.76, H 8.50, N 3.58, found: C 79.73, H 8.51, N 3.46.

6-(2-Fluor-4-(dodecyloxy)phenyl)indolin-2,3-dione (36)

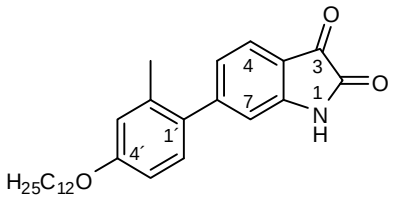


36

1.5 mmol (0.339 g) 6-bromoisatin and 1.65 mmol (0.535 g) of the boronic acid **6** have been converted and purified according to general procedure A yielding 0.270 g (42%) **36** as a orange solid. R_f=0.35 (SiO_2, DCM/MTBE 15:1); m.p. Cr 165 °C I (DCM/MTBE 15:1); ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ=8.19 (s, 1H; NH), 7.62 (d, ^3J=8.0 Hz, 1H; 4-H), 7.35 (m, 1H; 6′-H), 7.23 (d, ^3J=6.7 Hz, 1H; 5-H), 7.07 (s, 1H; 7-H), 6.78 (dd, ^3J=8.7 Hz, ^4J=2.4 Hz, 1H; 5′-H), 6.70 (dd, $^3J_{H,F}$=13.0 Hz, ^4J=2.4 Hz, 1H; 3′-H), 4.00 (t, ^3J=6.6 Hz, 2H; α-CH_2), 1.80 (m, 2H; β-CH_2),

1.46 (m, 2H; γ-CH_2), 1.40-1.22 (m, 16H; CH_2), 0.87 ppm (t, ^3J=6.9 Hz, 3H; CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$, 50 °C): δ=182.11 (s; C-3), 161.57 (s, $^3J_{C,F}$=11.4 Hz; C-4′), 160.65 (s, $^1J_{C,F}$=250.0 Hz; C-2′), 159.71 (s; C-2), 149.38 (s; C-7a), 146.70 (s; C-6), 130.73 (d, $^3J_{C,F}$=4.7 Hz; C-6′), 125.74 (d; C-4), 124.20 (d, $^4J_{C,F}$=3.2 Hz; C-5), 119.34 (s, $^2J_{C,F}$=13.1 Hz; C-1′), 116.81 (s; C-3a), 112.41 (d, $^4J_{C,F}$=4.5 Hz; C-7), 111.49 (d, $^4J_{C,F}$=2.8 Hz; C-5′), 102.98 (d, $^2J_{C,F}$=26.2 Hz; C-3′), 68.79 (t; α-CH_2), 31.92, 29.65, 29.62, 29.58, 29.55, 29.34, 29.32 (7 × t; CH_2), 29.11 (t; β-CH_2), 26.00 (t; γ-CH_2), 22.66 (t; CH_2), 14.02 ppm (q; CH_3); ^{19}F NMR (282.2 MHz, $CDCl_3$, 50 °C): δ=-113.58 ppm (m; 2′-F); IR (ATR): $\tilde{\nu}$=3276 (bm), 2915 (s), 2847 (s), 1762 (m), 1728 (s), 1614 (s), 1517 (w), 1469 (m), 1442 (w), 1425 (w), 1381 (w), 1341 (m), 1292 (s), 1225 (w), 1160 (s), 1118 (s), 997 (w), 953 (w), 896 (w), 845 (m), 815 (w), 799 (m), 729 (w), 715 (w), 692 (w), 653 cm^{-1} (m); UV/Vis (EtOH, 10 mg/L) λ_{max}: 250 (s), 346 nm (m); MS (EI, 70 eV) m/z (%): 425 (23) [M^+], 397 (5) [M^+ -CO], 257 (17) [M^+ -$C_{12}H_{25}$], 242 (14), 229 (100) [M^+ -$C_{12}H_{25}$ -CO], 202 (17) [M^+ -$C_{12}H_{25}$ -2CO], 173 (5), 157 (6); HRMS (EI, 70 eV): calcd for $C_{26}H_{32}FNO_3$ [M^+]: 425.2366, found: 425.236; elemental analysis calcd (%) for $C_{26}H_{32}FNO_3$: C 73.38, H 7.58, N 3.29, found: C *72.76*, H 7.61, N 3.07.

6-(4-(Dodecyloxy)-2-methylphenyl)indolin-2,3-dione (37)

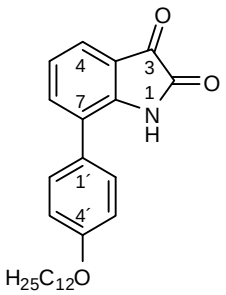


37

3.0 mmol (0.678 g) 6-bromoisatin and 4.0 mmol (1.280 g) of the boronic acid **7** have been converted and purified according to general procedure A yielding 1.136 g (90%) **37** as a orange solid. R_f=0.60 (SiO_2, DCM/MTBE 15:1); m.p. Cr 125 °C I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=9.04 (s, 1H; NH), 7.58 (d, ^3J=7.8 Hz, 1H; 4-H), 7.12 (d, ^3J=8.2 Hz, 1H; 6′-H), 7.01 (dd, ^3J=7.8 Hz, ^4J=1.2 Hz, 1H; 5-H), 6.90 (s, 1H; 7-H), 6.80 (s, 1H; 3′-H), 6.77 (dd, ^3J=9.8 Hz, ^4J=2.4 Hz, 1H; 5′-H), 3.97 (t, ^3J=6.5 Hz, 2H; α-CH_2), 2.28 (s, 3H; 2′-CH_3), 1.78 (m, 2H; β-CH_2), 1.45 (m, 2H; γ-CH_2), 1.38-1.18 (m, 16H; CH_2), 0.86 ppm (t, ^3J=6.6 Hz, 3H; alkyl-CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=182.64 (s; C-3), 160.33 (s; C-2), 159.34 (s; C-4′), 153.25 (s; C-6), 149.37 (s; C-7a), 136.53 (s; C-2′), 132.43 (s; C-1′), 130.42 (d; C-6′), 125.38 (d; C-5), 125.25 (d; C-4), 116.81 (s; C-3a), 116.17 (d; C-3′), 113.59 (d; C-7), 112.04 (d; C-5′), 68.03 (t; α-CH_2), 31.89, 29.57, 29.36, 29.32 (4 × t; CH_2), 29.23 (t; β-CH_2), 26.02 (t; γ-CH_2), 22.66 (t; CH_2), 20.73 (q; C-2′-CH_3), 14.09 ppm (q; alkyl-CH_3); IR (ATR): $\tilde{\nu}$=3285 (bw), 2911 (s), 2846 (m), 1763 (s), 1730 (s), 1613 (s), 1470 (m), 1434 (w), 1380 (w), 1336 (w), 1293 (m), 1231 (m), 1168 (w), 1119 (m), 1073 (w), 1043 (w), 1016 (w), 953 (w), 900

(w), 860 (w), 818 (w), 802 (w), 734 (w), 690 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 249 (s), 351 nm (m); MS (EI, 70 eV) m/z (%): 421 (26) [M^+], 253 (31) [M^+ -$C_{12}H_{25}$], 225 (100) [M^+ -$C_{12}H_{25}$ -CO], 197 (14) [M^+ -$C_{12}H_{25}$ -2CO], 170 (12), 141 (7), 115 (6), 83 (5), 71 (11), 69 (14), 55 (32); HRMS (EI, 70 eV): calcd for $C_{27}H_{35}NO_3$ [M^+]: 421.2617, found: 421.262; elemental analysis calcd (%) for $C_{27}H_{35}NO_3$: C 76.92, H 8.37, N 3.32, found: C 76.65, H 8.29, N 3.23.

7-(4-(Dodecyloxy)phenyl)indolin-2,3-dione (38)



38

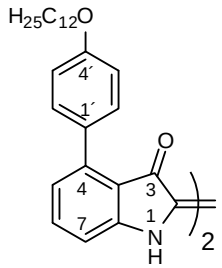
4.0 mmol (0.904 g) 7-bromoisatin and 4.0 mmol (1.280 g) of the boronic acid **5** have been converted and purified according to general procedure A yielding 1.478 g (90%) **38** as a orange solid. R_f=0.68 (SiO_2, DCM/MTBE 15:1); m.p. Cr 109.2 °C (23.6 kJ/mol) I (DCM/MTBE 15:1); ^{1}H NMR (300 MHz, DMSO, 25°C): δ=10.84 (s, 1H, NH), 7.52 (d, ^3J=7.7 Hz, 1H; 6-H), 7.47 (d, ^3J=7.4 Hz, 1H; 4-H), 7.38 (d, ^3J=8.4 Hz, 2H; 2′-H and 6′-H), 7.13 (t, ^3J=7.7 Hz, 1H; 5-H), 7.01 (d, ^3J=8.5 Hz, 2H; 3′-H and 5′-H), 4.00 (t, ^3J=6.3 Hz, 2H; α-CH_2), 1.75-1.68 (m, 2H; β-CH_2), 1.47-1.37 (m, 2H; γ-CH_2), 1.25 (m, 16H; CH_2), 0.85 ppm (t, ^3J=6.6 Hz, 3H; CH_3); ^{13}C NMR (75.5 MHz, DMSO, 25°C): δ=184.49 (s; C-3), 159.94 (s; C-2), 158.41 (s; C-4′), 147.32 (s; C-7a), 138.45 (d; C-6), 129.44 (d; C-2′ and C-6′), 127.42 (s; 1′-C), 125.62 (s; C-7), 123.06 (d; C-4), 122.99 (d; C-5), 118.41 (s; C-3a), 114.72 (d; C-3′ and C-5′), 67.41 (t; α-CH_2), 31.24, 28.97, 28.74, 28.67, 28.60 (5 × t; CH_2), 25.46 (t; γ-CH_2), 22.03 (t; CH_2), 13.83 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=3256 (bm), 2920 (s), 2850 (m), 1758 (s), 1736 (s), 1607 (s), 1514 (m), 1483 (m), 1436 (m), 1407 (w), 1377 (w), 1324 (w), 1246 (s), 1179 (m), 1110 (w), 1026 (w), 956 (w), 834 (w), 824 (w), 778 (w), 732 (m), 700 (m), 614 cm^{-1} (w); UV/Vis (EtOH, 10 mg/L) λ_{max}: 248 (s), 428 nm (w); MS (EI, 70 eV) m/z (%): 407 (32) [M^+], 239 (17) [M^+-$C_{12}H_{25}$], 211 (7) [M^+-$C_{12}H_{25}$, -CO], 183 (100) [M^+-$C_{12}H_{25}$, -2CO], 154 (14), 139 (5), 127 (7), 83 (6), 69 (14), 57 (25), 55 (26); HRMS (EI, 70 eV): calcd for $C_{26}H_{33}NO_3$ [M^+]: 407.2461, found: 407.245;elemental analysis calcd (%) for $C_{26}H_{33}NO_3$: C 76.62, H 8.16, N 3.44, found: C 76.56, H 8.15, N 3.27.

Syntheses of the *N,N´*-unsubstituted Indigo Derivatives (Type III):

General procedure B:

To a 0.1 molar solution of the isatin derivative in dry toluene 1.05 eq. phosphorous pentachloride were given and the reaction was heated to 100 °C for 4 hours under argon atmosphere. Subsequently the dark red reaction mixture was cooled to 50 °C, 2.2 eq. thiophenol were added and kept on this temperature for 16 hours. To the dark solution 1.5 times the volume of methanol was given to precipitate the crude product, which was filtered off as a coloured solid. Most of these solid were insoluble and could not be purified further or solved for analytic purpose.

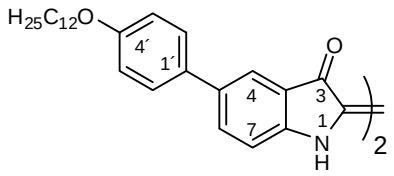
4,4´-Bis-(4-(dodecyloxy)phenyl)indigo (8)



8

After reacting 0.50 mmol (0.204 g) **29** according to general procedure B the crude product was purified chromatographically (silica gel, DCM/cyclohexane 2:1), yielding 0.091 g (46%) **8** as a blue solid. R_f=0.31 (SiO_2, *c*Hex/DCM 2:1); m.p. Cr 253.1 °C (37.6 kJ/mol) I (*c*Hex/DCM 2:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=9.04 (s, 2H; NH), 7.53 (d, ^3J=8.7 Hz, 4H; 2´-H and 6´-H), 7.42 (t, ^3J=7.8 Hz, 2H; 6-H), 6.98 (d, ^3J=8.7 Hz, 4H; 3´-H and 5´-H), 6.87 (d, ^3J=7.4 Hz, 2H; 5-H), 6.83 (d, ^3J=8.0 Hz, 2H; 7-H), 4.01 (t, ^3J=6.5 Hz, 4H; α-CH_2), 1.80 (m, 4H; β-CH_2), 1.47 (m, 4H; γ-CH_2), 1.40-1.18 (m, 32H; CH_2), 0.87 ppm (t, ^3J=6.7 Hz, 6H; CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25°C): δ=187.88 (s; C-3), 159.49 (s; C-4´), 152.64 (s; C-7a), 142.24 (s; C-4), 135.57 (d; C-6), 130.38 (d; C-2´and C-6´), 129.30 (s; C-1´), 122.32 (d; C-5), 121.63 (s; C-2), 115.95 (s; C-3a), 113.70 (d; C-3´and C-5´), 110.38 (s; C-7), 67.89 (t; α-CH_2), 29.36 (t; CH_2), 29.25 (t; β-CH_2), 26.07 (t; γ-CH_2), 22.71 (t; CH_2), 14.18 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$ =2915 (s), 2848 (m), 1635 (m), 1599 (s), 1516 (w), 1486 (m), 1414 (w), 1392 (m), 1300 (w), 1221 (s), 1173 (s), 1080 (s), 1049 (m), 918 (m), 831 (w), 799 (m), 770 (m), 701 (m), 617 cm^{-1} (w); UV/Vis (NMP, 10 mg/L) λ_{max}: 306 (m), 634 nm (m); MS (EI, 70 eV) m/z (%): 783 (9) [M^+], 615 (2) [M^+-$C_{12}H_{25}$], 446 (6) [M^+-2$C_{12}H_{25}$], 418 (3), 401 (4), 250 (3), 225 (6), 196 (9), 168 (11), 139 (12), 84 (50), 57 (100); elemental analysis calcd (%) for $C_{52}H_{66}N_2O_4$, C 79.76, H 8.50, N 3.58, found: C 79.31, H 8.58, N 3.43.

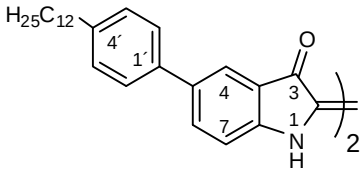
5,5´-Bis-(4-(dodecyloxy)phenyl)indigo (9)



9

After reacting 2.42 mmol (0.986 g) **30** according to general procedure B the crude product was filtered off, yielding 0.650 g (69%) **11** as a violet solid. m.p. decomp. at 350 °C, before smectic (MeOH/toluene); IR (ATR): $\tilde{\nu}$=3359 (w), 2916 (s), 2848 (m), 1731 (w), 1694 (w), 1635 (s), 1622 (s), 1561 (w), 1517 (w), 1472 (m), 1448 (m), 1268 (s), 1252 (m), 1203 (m), 1144 (m), 1028 (w), 814 (s), 727 (w), 672 cm^{-1} (w); UV/Vis (NMP, 10 mg/L) λ_{max}: 285 (s), 647 nm (m).

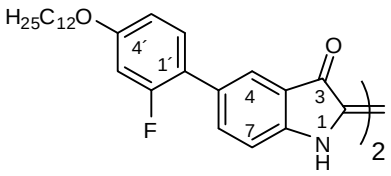
5,5´-Bis-(4-dodecylphenyl)indigo (14)



14

After reacting 1.00 mmol (0.391 g) **31** according to general procedure B the crude product was filtered off, yielding 0.166 g (44%) **14** as a violet solid. m.p. decomp. at 326 °C, before smectic (MeOH/toluene); IR (ATR): $\tilde{\nu}$=3374 (w), 2915 (s), 2847 (m), 1626 (s), 1612 (s), 1586 (w), 1470 (m), 1447 (m), 1406 (w), 1260 (w), 1189 (w), 1137 (s), 1073 (w), 812 (m), 783 (w), 717 (w), 669 cm^{-1} (m); UV/Vis (NMP, 10 mg/L) λ_{max}: 641 nm (m).

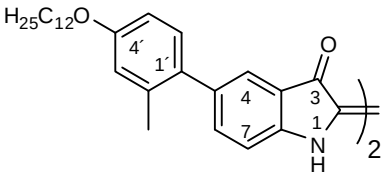
5,5´-Bis-(2-fluoro-4-(dodecyloxy)phenyl)indigo (15)



15

After reacting 1.00 mmol (0.425 g) **32** according to general procedure B the crude product was suspended in boiling ethyl acetate applying ultrasound and filtered off after cooling to room temperature yielding 0.321 g (78%) **15** as a blue solid. m.p. Cr 116.6 (38.3) SC 322.9 °C (36.5 kJ/mol) I, Decomp. (EtOAc); IR (ATR): $\tilde{\nu}$=3373 (m), 2916 (s), 2850 (m), 1637 (s), 1622 (s), 1573 (w), 1516 (w), 1466 (m), 1449 (m), 1406 (w), 1320 (w), 1278 (m), 1230 (w), 1199 (m), 1162 (m), 1141 (m), 1119 (m), 1076 (w), 1036 (w), 1003 (w), 956 (w), 896 (w), 838 (m), 818 (m), 811 (m), 746 (w), 721 (w), 669 cm^{-1} (m); elemental analysis calcd (%) for $C_{52}H_{64}F_2N_2O_4$: C 76.25, H 7.88, N 3.42, gef.: C *75.55*, H 7.97, N 3.44.

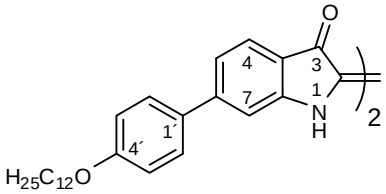
5,5´-Bis-(4-(dodecyloxy)-2-methylphenyl)indigo (16)



16

After reacting 1.00 mmol (0.421 g) **33** according to general procedure B the crude product was suspended in boiling ethyl acetate applying ultrasound and filtered off after cooling to room temperature yielding 0.267 g (66%) **16** as a blue solid. m.p. Cr 241.4 (4.4) SC 168.6 °C (56.6 kJ/mol) I (EtOAc); IR (ATR): $\tilde{\nu}$=3356 (w), 2916 (s), 2851 (m), 1630 (s), 1609 (s), 1563 (w), 1471 (s), 1394 (w), 1291 (m), 1233 (m), 1187 (s), 1146 (m), 1120 (s), 1074 (m), 1050 (m), 906 (w), 864 (w), 833 (m), 810 (m), 782 (m), 734 (w), 716 (w), 670 cm^{-1} (w); UV/Vis (NMP, 10 mg/L) λ_{max}: 633 nm (m); elemental analysis calcd (%) for $C_{54}H_{70}N_2O_4$: C 79.96, H 8.70, N 3.45, gef.: C *79.40*, H 8.71, N 3.48.

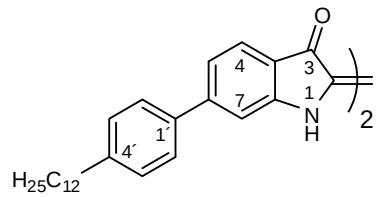
6,6´-Bis-(4-(dodecyloxy)phenyl)indigo (10)



10

After reacting 2.00 mmol (0.815 g) **34** according to general procedure B the crude product was filtered off, yielding 0.297 g (38%) **10** as a dark green solid. m.p. Decomp. at 320 °C (MeOH/toluene); IR (ATR): $\tilde{\nu}$ =3308 (w), 2917 (s), 2848 (s), 1604 (m), 1518 (m), 1466 (w), 1448 (w), 1378 (w), 1247 (w), 1176 (w), 1143 (w), 1110 (w), 1034 (w), 820 (w), 779 (w), 719 (w), 707 cm^{-1} (w); UV/Vis (NMP, 10 mg/L) λ_{max}: 316 (s), 405 (s); 618 nm (m).

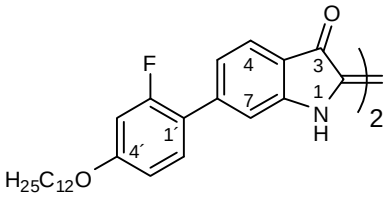
6,6´-Bis-(4-dodecylphenyl)indigo (20)



20

After reacting 1.00 mmol (0.391 g) **35** according to general procedure B the crude product was filtered off, yielding 0.122 g (33%) **20** as a dark green solid. m.p. Decomp. at 320 °C (MeOH/toluene); IR (ATR): $\tilde{\nu}$ =3293 (w), 2916 (s), 2847 (s), 1613 (s), 1560 (m), 1520 (w), 1463 (w), 1447 (m), 1380 (w), 1338 (m), 1303 (w), 1180 (w), 1143 (m), 1110 (m), 1080 (w), 1006 (w), 916 (w), 870 (w), 843 (w), 809 (w), 776 (w), 746 (w), 705 cm^{-1} (w).

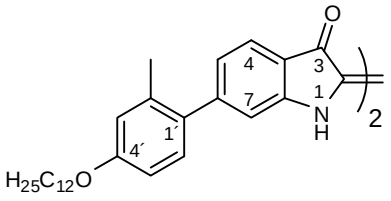
6,6´-Bis-(2-fluoro-4-(dodecyloxy)phenyl)indigo (21)



21

After reacting 0.50 mmol (0.213 g) **36** according to general procedure B the crude product was suspended in boiling ethyl acetate applying ultrasound and filtered off after cooling to room temperature yielding 0.119 g (58%) **21** as a green solid. m.p. Cr 239.2 (7.9) SmF/I 296.8 °C (56.1 kJ/mol) I (EtOAc); IR (ATR): $\tilde{\nu}$=3326 (w), 2917 (m), 2846 (m), 1609 (s), 1576 (m), 1513 (m), 1463 (w), 1444 (m), 1384 (w), 1314 (m), 1283 (m), 1233 (m), 1160 (m), 1132 (s), 1076 (m), 1010 (w), 956 (w), 903 (w), 873 (w), 829 (m), 782 (w), 746 (m), 704 cm^{-1} (m); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 341 (m), 619 nm (m); elemental analysis calcd (%) for $C_{52}H_{64}F_2N_2O_4$: C 76.25, H 7.88, N 3.42, found: C 76.44, H 8.04, N 3.49.

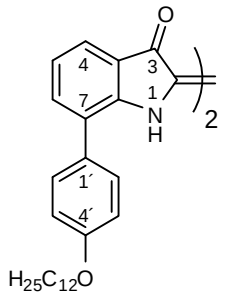
6,6´-Bis-(4-(dodecyloxy)-2-methylphenyl)indigo (22)



22

After reacting 1.50 mmol (0.632 g) **37** according to general procedure B the crude product was suspended in boiling ethyl acetate applying ultrasound and filtered off after cooling to room temperature yielding 0.459 g (75%) **22** as a green solid. m.p. Cr 141.0 (20.5) SmF/I 263.8 °C (44.2 kJ/mol) I (EtOAc); IR (ATR): $\tilde{\nu}$=3334 (w), 2915 (m), 2848 (m), 1607 (s), 1576 (m), 1509 (m), 1463 (w), 1441 (s), 1383 (w), 1307 (m), 1286 (m), 1230 (m), 1200 (w), 1166 (w), 1130 (s), 1113 (s), 1077 (m), 1040 (w), 1012 (w), 896 (w), 843 (w), 783 (m), 744 (w), 707 cm^{-1} (m); UV/Vis ($CHCl_3$, 20 mg/L) λ_{max}: 292 (s), 398 (m), 604 nm (m); elemental analysis calcd (%) for $C_{54}H_{70}N_2O_4$: C 79.96, H 8.70, N 3.45, found: C 79.69, H 8.67, N 3.37.

7,7´-Bis-(4-(dodecyloxy)phenyl)indigo (11)



11

After reacting 2.00 mmol (0.815 g) **38** according to general procedure B the crude product was purified chromatographically (silica gel, DCM/cyclohexane 1:1), yielding 0.426 g (54%) **11** as a blue solid. R_f=0.31 (SiO_2, *c*Hex/DCM 1:1); m.p. Cr 217.8 °C (30.1 kJ/mol) I (*c*Hex/DCM 1:1); ^{1}H NMR

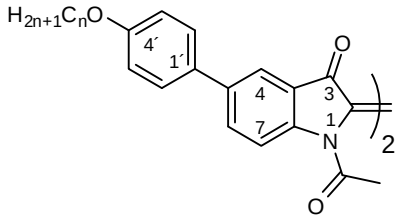
(300 MHz, $CDCl_3$, 25°C): δ=9.08 (s, 2H; NH), 7.62 (d, ^3J=7.6 Hz, 2H; 4-H), 7.47 (d, ^3J=8.4 Hz, 4H; 2´-H and 6´-H), 7.44 (d, ^3J=7.2 Hz, 2H; 6-H), 7.05 (d, ^3J=8.5 Hz, 4H; 3´-H and 5´-H), 7.00 (t, ^3J=7.7 Hz, 2H; 5-H), 4.02 (t, ^3J=6.5 Hz, 4H; α-CH_2), 1.83 (m, 4H; β-CH_2), 1.49 (m, 4H; γ-CH_2), 1.41-1.18 (m, 32H; CH_2), 0.87 ppm (t, ^3J=6.6 Hz, 6H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=188.82 (s; C-3), 159.22 (s; C-4´), 149.11 (s; C-7a), 135.42 (d; C-6), 128.75 (d; C-2´and C-6´), 128.26 (s; C-1´), 126.19 (s; C-7), 122.75 (d; C-4), 121.53 (s; C-2), 121.27 (d; C-5), 120.33 (s; C-3a), 115.50 (d; C-3´and C-5´), 68.16 (t; α-CH_2), 31.92, 29.68, 29.62, 29.42, 29.36 (5 × t; CH_2), 29.28 (t; β-CH_2), 26.08 (t; γ-CH_2), 22.69 (t; CH_2), 14.12 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=2918 (m), 2849 (s), 1635 (s), 1602 (m), 1513 (w), 1483 (m), 1430 (w), 1409 (m), 1300 (w), 1282 (m), 1248 (m), 1146 (s), 1094 (m), 1052 (w), 1021 (w), 837 (w), 807 (w), 757 (w), 708 cm^{-1} (w); UV/Vis (NMP, 10 mg/L) λ_{max}: 314 (s), 621 nm (m); MS (EI, 70 eV) m/z (%): 783 (15) [M^+], 613 (3) [M^+-$C_{12}H_{25}$], 446 (8) [M^+-2$C_{12}H_{25}$], 417 (6), 218 (3), 196 (7), 139 (6), 109 (6), 84 (26), 71 (37), 57 (100); elemental analysis calcd (%) for $C_{52}H_{66}N_2O_4$, C 79.76, H 8.50, N 3.58, found: C 79.41, H 8.47, N 3.46.

Syntheses of the *N,N´*-diacetylated Indigo Derivates (Type IV):

General procedure C:

1 eq. of the *N,N´*-unsubstituted indigo derivative was suspended in 50 times the amount of dry NMP and treated with 50 eq. acetic anhydride and 50 eq. acetyl chloride. The reaction suspension was stirred for 6 hours at 90 °C under argon atmosphere. After adding twice the amount of water and ethyl acetate, the organic phase was separated and washed five times with water and once with saturated sodium carbonate solution and dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product was purified chromatographically (silica gel, DCM) and finally recrystallised from ethanol.

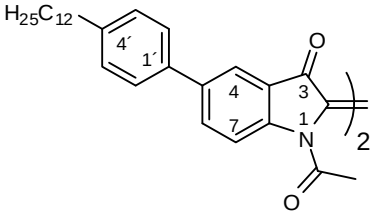
***N,N´*-Diacetyl-5,5´-bis-(4-(dodecyloxy)phenyl)indigo (12)**



12

0.50 mmol (0.391 g) **9** have been converted and purified according to general procedure C yielding 0.324 g (75%) **12** as a violet solid. R_f=0.34 (SiO_2, *c*Hex/EtOAc 3:1); m.p. Cr 124.8 (53.2) Cr_2 160.5 °C (26.7 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.26 (d, ^3J=8.4 Hz, 2H; 7-H), 7.89 (d, ^4J=1.7 Hz, 2H; 4-H), 7.82 (dd, ^3J=8.6 Hz, ^4J=1.9 Hz, 2H; 6-H), 7.48 (d, ^3J=8.7 Hz, 4H; 2´-H and 6´-H), 6.95 (d, ^3J=8.7 Hz, 4H; 3´-H and 5´-H), 3.98 (t, ^3J=6.5 Hz, 4H; *α*-CH_2), 2.57 (s, 6H; $NCOCH_3$), 1.79 (m, 4H; *β*-CH_2), 1.45 (m, 4H; *γ*-CH_2), 1.38-1.20 (m, 32H; CH_2), 0.86 ppm (t, ^3J=6.5 Hz, 6H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=184.19 (s; C-3), 169.96 (s; N*C*OCH_3), 159.22 (s; C-4´), 147.78 (s; C-7a), 138.34 (s; C-5), 135.09 (d; C-6), 131.23 (s; C-1´), 127.89 (d; C-2´and C-6´), 126.53 (s; C-2), 122.45 (s; C-3a), 121.64 (d; C-4), 117.46 (d; C-7), 115.02 (d; C-3´and C-5´), 68.15 (t; *α*-CH_2), 31.90, 29.62, 29.58, 29.38, 29.33 (5 × t; CH_2), 29.22 (t; *β*-CH_2), 26.02 (t; *γ*-CH_2), 23.88 (q; NCO*C*H_3), 22.67 (t; CH_2), 14.10 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=2921 (m), 2851 (m), 1707 (m), 1676 (s), 1608 (m), 1520 (w), 1470 (s), 1360 (w), 1298 (m), 1268 (m), 1245 (s), 1179 (m), 1115 (m), 1071 (s), 1029 (m), 929 (w), 822 (m), 789 (w), 777 (w), 718 (w), 646 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 289 (s), 345 (m), 579 nm (m); elemental analysis calcd (%) for $C_{56}H_{70}N_2O_6$: C 77.56, H 8.14, N 3.23, found: C 77.78, H 8.17, N 3.15.

***N,N´*-Diacetyl-5,5´-bis-(4-dodecylphenyl)indigo (17)**

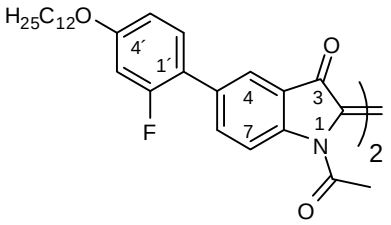


17

0.15 mmol (0.113 g) **14** have been converted and purified according to general procedure C yielding 0.113 g (87%) **17** as a violet solid. R_f=0.43 (SiO_2, *c*Hex/EtOAc 3:1); m.p. Cr 106.8 °C (56.2 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.29 d, ^3J=8.3 Hz, 2H; 7-H), 7.94 (d, ^4J=1.7 Hz, 2H; 4-H), 7.87 (dd, ^3J=8.6 Hz, ^4J=2.0 Hz, 2H; 6-H), 7.48 (d, ^3J=8.1 Hz, 4H; 2´-H and 6´-H), 7.25 (d, ^3J=8.0 Hz, 4H; 3´-H and 5´-H), 2.63 (t, ^3J=7.7 Hz, 4H; *α*-CH_2), 2.58 (s, 6H; $NCOCH_3$), 1.62 (m, 4H; *β*-CH_2), 1.38-1.18 (m, 36H; CH_2), 0.86 ppm (t, ^3J=6.6 Hz, 6H; CH_3);^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=184.15 (s; C-3), 169.95 (s; N*C*OCH_3), 148.05 (s; C-7a), 142.98 (s; C-4´), 138.57 (s; C-5), 136.28 (s; C-1´), 135.41 (d; C-6), 129.09 (d; C-3´and C-5´), 126.68 (d; C-2´and C-6´), 122.43 (s; C-3a), 122.03 (d; C-4),

117.47 (d; C-7), 35.59 (t; α-CH_2), 31.90 (t; CH_2), 31.46 (t; β-CH_2), 29.65, 29.50, 29.33 (3 × t; CH_2), 23.89 (q; NCO*C*H_3), 22.68 (t; CH_2), 14.12 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=2922 (s), 2851 (m), 1707 (m), 1679 (s), 1612 (m), 1472 (s), 1435 (w), 1360 (m), 1303 (m), 1284 (m), 1235 (w), 1187 (m), 1169 (m), 1115 (m), 1071 (m), 1026 (w), 1004 (w), 930 (w), 828 (w), 777 (w), 718 (w), 616 cm^{-1} (s); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 284 (m), 343 (m), 572 nm (m); elemental analysis calcd (%) for $C_{56}H_{70}N_2O_4$: C 80.53, H 8.45, N 3.35, found: C 80.48, H 8.43, N 3.29.

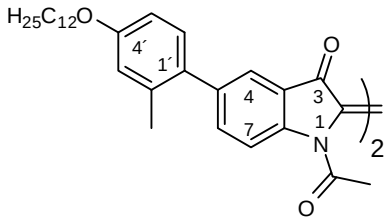
***N,N´*-Diacetyl-5,5´-bis-(2-fluoro-4-(dodecyloxy)phenyl)indigo (18)**



18

0.12 mmol (0.100 g) **15** have been converted and purified according to general procedure C yielding 0.038 g (34%) **18** as a violet solid. R_f=0.23 (SiO_2, DCM); m.p. Cr 170.9 °C (32.6 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.27 (d, ^3J=8.3 Hz, 2H; 7-H), 7.87 (s, 2H; 4-H), 7.78 (d, ^3J=8.7 Hz, 2H; 6-H), 7.30 (m, 2H; 6´-H), 6.75 (dd, ^3J=8.6 Hz, ^4J=2.0 Hz, 2H; 5´-H), 6.68 (dd, $^3J_{H,F}$=12.7 Hz, ^4J=2.2 Hz, 2H; 3´-H), 3.96 (t, ^3J=6.5 Hz, 4H; α-CH_2), 2.56 (s, 6H; NCOCH_3), 1.78 (m, 4H; β-CH_2), 1.44 (m, 4H; γ-CH_2), 1.38-1.20 (m, 32H; CH_2), 0.86 ppm (t, ^3J=6.5 Hz, 6H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=184.02 (s; C-3), 169.92 (s; N*C*OCH_3), 160.35 (s, $^3J_{C,F}$=10.9 Hz; C-4´), 160. 23 (s, $^1J_{C,F}$=248.0 Hz; C-2´), 147.94 (s; C-7a), 137.19 (d; C-6), 133.20 (s; C-5), 130.54 (d, $^3J_{C,F}$=4.5 Hz; C-6´), 126.44 (s; C-2), 124.09 (d; C-4), 122.13 (s; C-3a), 119.00 (s, $^2J_{C,F}$=13.5 Hz; C-1´), 117.13 (d; C-7), 111.09 (d; C-5´), 102.61 (s, $^2J_{C,F}$=26.1 Hz; C-3´), 68.51 (t; α-CH_2), 31.90, 29.62, 29.57, 29.33 (4 × t; CH_2), 29.07 (t; β-CH_2), 25.96 (t; γ-CH_2), 23.88 (q; NCO*C*H_3), 22.67 (t; CH_2), 14.10 ppm (q; CH_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=-115.61 ppm (m; 2´-F); IR (ATR): $\tilde{\nu}$=2921 (s), 2846 (m), 1707 (s), 1679 (s), 1617 (s), 1568 (w), 1514 (w), 1469 (s), 1361 (m), 1310 (m), 1285 (s), 1225 (m), 1172 (s), 1120 (s), 1071 (s), 1028 (w), 929 (w), 837 (w), 722 (w), 623 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 287 (s), 340 (s), 570 nm (m); elemental analysis calcd (%) for $C_{56}H_{68}F_2N_2O_6$: C 74.47, H 7.59, N 3.10, found: C 74.10, H 7.75, N 3.09.

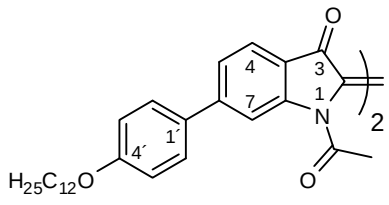
***N,N´*-Diacetyl-5,5´-bis-(4-(dodecyloxy)-2-methylphenyl)indigo (19)**



19

0.19 mmol (0.150 g) **16** have been converted and purified according to general procedure C yielding 0.130 g (78%) **19** as a red-violet solid. R_f=0.30 (SiO_2, DCM); m.p. Cr 110.6 °C (47.2 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.27 (d, ^3J=8.4 Hz, 2H; 7-H), 7.68 (d, ^4J=1.6 Hz, 2H; 4-H), 7.58 (dd, ^3J=8.5 Hz, ^4J=1.9 Hz, 2H; 6-H), 7.09 (d, ^3J=8.3 Hz, 2H; 6´-H), 6.79 (s, 2H; 3´-H), 6.76 (dd, ^3J=8.6 Hz, ^4J=2.4 Hz, 2H; 5´-H), 3.96 (t, ^3J=6.5 Hz, 4H; α-CH_2), 2.58 (s, 6H; $NCOCH_3$), 2.21 (s, 6H; 2´-CH_3), 1.78 (m, 4H; β-CH_2), 1.45 (m, 4H; γ-CH_2), 1.38-1.18 (m, 32H; CH_2), 0.86 ppm (t, ^3J=6.5 Hz, 6H; alkyl-CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=184.13 (s; C-3), 169.95 (s; N*C*OCH_3), 158.82 (s; C-4´), 147.73 (s; C-7a), 139.10 (s; C-5), 138.02 (d; C-6), 136.59 (s; C-2´), 132.09 (s; C-1´), 130.69 (d; C-6´), 126.56 (s; C-2), 124.57 (d; C-4), 121.87 (s; C-3a), 116.89 (d; C-7), 116.56 (d; C-3´), 111.95 (d; C-5´), 68.01 (t; α-CH_2), 31.90, 29.59, 29.38, 29.34 (4 × t; CH_2), 29.28 (t; β-CH_2), 26.04 (t; γ-CH_2), 23.90 (q; NCO*C*H_3), 22.68 (t; CH_2), 20.67 (q; C-2´-*C*H_3), 14.11 ppm (q; alkyl-CH_3); IR (ATR): $\tilde{\nu}$=2920 (s), 2850 (m), 1708 (m), 1680 (s), 1610 (m), 1566 (w), 1469 (s), 1360 (w), 1268 (s), 1231 (s), 1186 (m), 1170 (s), 1114 (m), 1068 (s), 928 (m), 840 (w), 813 (w), 778 (w), 721 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 279 (s), 569 nm (m); elemental analysis calcd (%) for $C_{58}H_{74}N_2O_6$: C 77.82, H 8.33, N 3.13, found: C 77.95, H 8.34, N 3.09.

***N,N´*-Diacetyl-6,6´-bis-(4-(dodecyloxy)phenyl)indigo (13)**

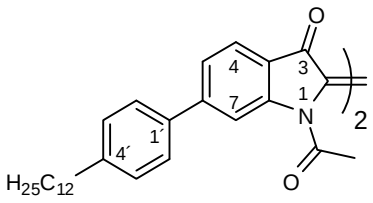


13

0.13 mmol (0.100 g) **10** have been converted and purified according to general procedure C yielding 0.065 g (60%) **13** as a red solid. R_f=0.14/0.31 (SiO_2, *c*Hex/EtOAc 3:1); m.p. Cr 180.6 (10.7) SmA 203.9 °C (7.0 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.49 (s, 2H; 7-H), 7.76 (d, ^3J=8.0 Hz, 2H; 4-H), 7.61 (d, ^3J=8.8 Hz, 4H; 2´-H and 6´-H), 7.44 (dd, ^3J=8.0 Hz, ^4J=1.3 Hz, 2H; 5-H), 6.97 (d, ^3J=8.8 Hz, 4H; 3´-H and 5´-H), 4.00 (t, ^3J=6.5 Hz, 4H; α-CH_2), 2.57 (s, 6H; $NCOCH_3$), 1.80 (m, 4H; β-CH_2), 1.46 (m, 4H; γ-CH_2), 1.40-1.18 (m, 32H; CH_2), 0.87 ppm (t, ^3J=6.6 Hz, 6H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=183.43 (s; C-3), 170.24 (s; N*C*OCH_3), 160.19 (s; C-4´), 149.90 [two signals: (s; C-6) and (s; C-7a)], 131.82 (s; C1´), 128.83 (d; C-2´and C-

6´), 127.00 (s; C-2), 124.64 (d; C-4), 123.62 (d; C-5), 120.12 (s; C-3a), 115.05 (d; C-3´and C-5´), 114.85 (d, C-7), 68.23 (t; α-CH_2), 31.95, 29.67, 29.63, 29.42, 29.38 (5 × t; CH_2), 29.25 (t; β-CH_2), 26.06 (t; γ-CH_2), 24.05 (q; NCO*C*H_3), 21.92 (t; CH_2), 14.15 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=2921 (s), 2850 (m), 1707 (m), 1672 (m), 1598 (s), 1570 (w), 1518 (m), 1468 (m), 1433 (m), 1405 (m), 1363 (m), 1328 (w), 1302 (m), 1243 (s), 1177 (s), 1108 (m), 1070 (m), 1003 (w), 969 (w), 934 (w), 914 (w), 889 (w), 823 (m), 776 (m), 713 (w), 688 (w), 654 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 258 (m), 289 (m), 415 nm (m); elemental analysis calcd (%) for $C_{56}H_{70}N_2O_6$: C 77.56, H 8.14, N 3.23, found: C 77.64, H 8.16, N 3.17.

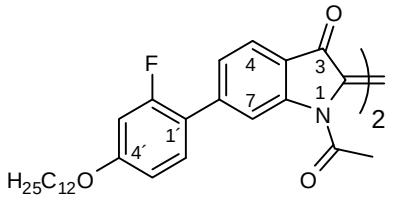
***N,N´*-Diacetyl-6,6´-bis-(4-dodecylphenyl)indigo (23)**



23

0.15 mmol (0.113 g) **20** have been converted and purified according to general procedure C yielding 0.123 g (95%) **23** as a red solid. R_f=0.33/0.48 (SiO_2, *c*Hex/EtOAc 3:1); m.p. Cr 99.2 (18.8) Cr_2 168.1 (7.6) SmA 178.0 °C (6.9 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.52 (s, 2H; 7-H), 7.78 (d, ^3J=8.0 Hz, 2H; 4-H), 7.58 (d, ^3J=8.1 Hz, 4H; 2´-H and 6´-H), 7.47 (dd, ^3J=8.0 Hz, ^4J=1.2 Hz, 2H; 5-H), 7.28 (d, ^3J=8.1 Hz, 4H; 3´-H and 5´-H), 2.65 (t, ^3J=7.8 Hz, 4H; α-CH_2), 2.57 (s, 6H; $NCOCH_3$), 1.64 (m, 4H; β-CH_2), 1.38-1.18 (m, 36H; CH_2), 0.86 ppm (t, ^3J=7.8 Hz, 6H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=183.52 (s; C-3), 170.15 (s; N*C*OCH_3), 150.22 (s; C-6), 149.80 (s; C-7a), 144.25 (s; C-4´), 137.00 (s; C1´), 129.11 (d; C-3´and C-5´), 127.47 (d; C-2´and C-6´), 126.87 (s; C-2), 124.59, 124.04 [two signals: (d; C-4) and (d; C-5)], 120.43 (s; C-3a), 115.34 (d, C-7), 35.69 (t; α-CH_2), 31.92 (t; CH_2), 31.40 (t; β-CH_2), 29.80, 29.67, 29.59, 29.51, 29.35 (5 × t; CH_2), 24.01 (q; NCO*C*H_3), 22.69 (t; CH_2), 14.13 ppm (q; CH_3); IR (ATR): $\tilde{\nu}$=2921 (s), 2851 (s), 1699 (s), 1602 (s), 1561 (m), 1463 (w), 1431 (m), 1402 (m), 1363 (m), 1302 (m), 1240 (m), 1181 (w), 1096 (s), 1068 (w), 1005 (w), 969 (w), 915 (w), 888 (w), 822 (w), 776 (w), 718 (w), 688 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 253 (m), 311 (m), 381 nm (m); elemental analysis calcd (%) for $C_{56}H_{70}N_2O_4$: C 80.53, H 8.45, N 3.35, found: C 80.53, H 8.42, N 3.30.

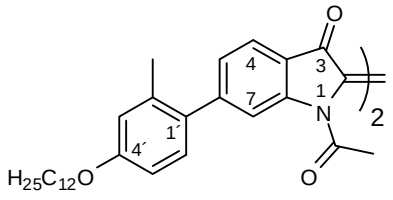
***N,N´*-Diacetyl-6,6´-bis-(2-fluoro-4-(dodecyloxy)phenyl)indigo (24)**



24

0.10 mmol (0.081 g) **21** have been converted and purified according to general procedure C yielding 0.058 g (73%) **24** as a red solid. R_f=0.07/0.23 (SiO_2, DCM); m.p. Cr 140.7 (15.5) SmA 145.9 (1.3) N 149.3 °C (1.9 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.41 (s, 2H; 7-H), 7.77 (d, ^3J=8.0 Hz, 2H; 4-H), 7.41 (d, ^3J=8.4 Hz, 2H; 5-H), 7.40 (m, 2H; 6´-H), 6.78 (dd, ^3J=8.5 Hz, ^4J=2.2 Hz, 2H; 5´-H), 6.70 (dd, $^3J_{H,F}$=12.7 Hz, ^4J=2.3 Hz, 2H; 3´-H), 3.98 (t, ^3J=6.5 Hz, 4H; α-CH_2), 2.56 (s, 6H; $NCOCH_3$), 1.79 (m, 4H; β-CH_2), 1.45 (m, 4H; γ-CH_2), 1.38-1.20 (m, 32H; CH_2), 0.86 ppm (t, ^3J=6.6 Hz, 6H; CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=183.51 (s; C-3), 170.06 (s; N*C*OCH_3), 161.08 (s, $^3J_{C,F}$=11.5 Hz; C-4´), 160.44 (s, $^1J_{C,F}$=249.9 Hz; C-2´), 149.40 (s; C-7a), 144.96 (s; C-6), 131.14 (d, $^3J_{C,F}$=4.5 Hz; C-6´), 126.70 (s; C-2), 125.87 (d; C-5), 124.14 (d; C-4), 120.42 (s; C-3a), 119.81 (s, $^2J_{C,F}$=13.0 Hz; C-1´), 117.05 (d; C-7), 111.17 (d; C-5´), 102.68 (d, $^2J_{C,F}$=26.0 Hz; C-3´), 68.57 (t; α-CH_2), 31.90, 29.63, 29.58, 29.34 (4 × t; CH_2), 29.05 (t; β-CH_2), 25.96 (t; γ-CH_2), 23.99 (q; NCO*C*H_3), 22.68 (t; CH_2), 14.11 ppm (q; CH_3); ^{19}F NMR (282.2 MHz, $CDCl_3$, 25 °C): δ=-114.02 ppm (m; 2´-F); IR (ATR): $\tilde{\nu}$ =2919 (s), 2850 (m), 1702 (m), 1604 (s), 1565 (m), 1548 (m), 1514 (m), 1466 (m), 1432 (w), 1410 (m), 1363 (m), 1323 (s), 1289 (s), 1228 (m), 1184 (m), 1164 (m), 1095 (s), 1034 (w), 1004 (w), 970 (m), 909 (w), 875 (w), 848 (w), 831 (w), 769 (w), 746 (w), 715 (w), 688 (w), 647 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 256 (s), 311 (m), 381 nm (m); elemental analysis calcd (%) for $C_{56}H_{68}F_2N_2O_6$: C 74.47, H 7.59, N 3.10, found: C 74.46, H 7.62, N 3.10.

***N,N´*-Diacetyl-6,6´-bis-(4-(dodecyloxy)-2-methylphenyl)indigo (25)**



25

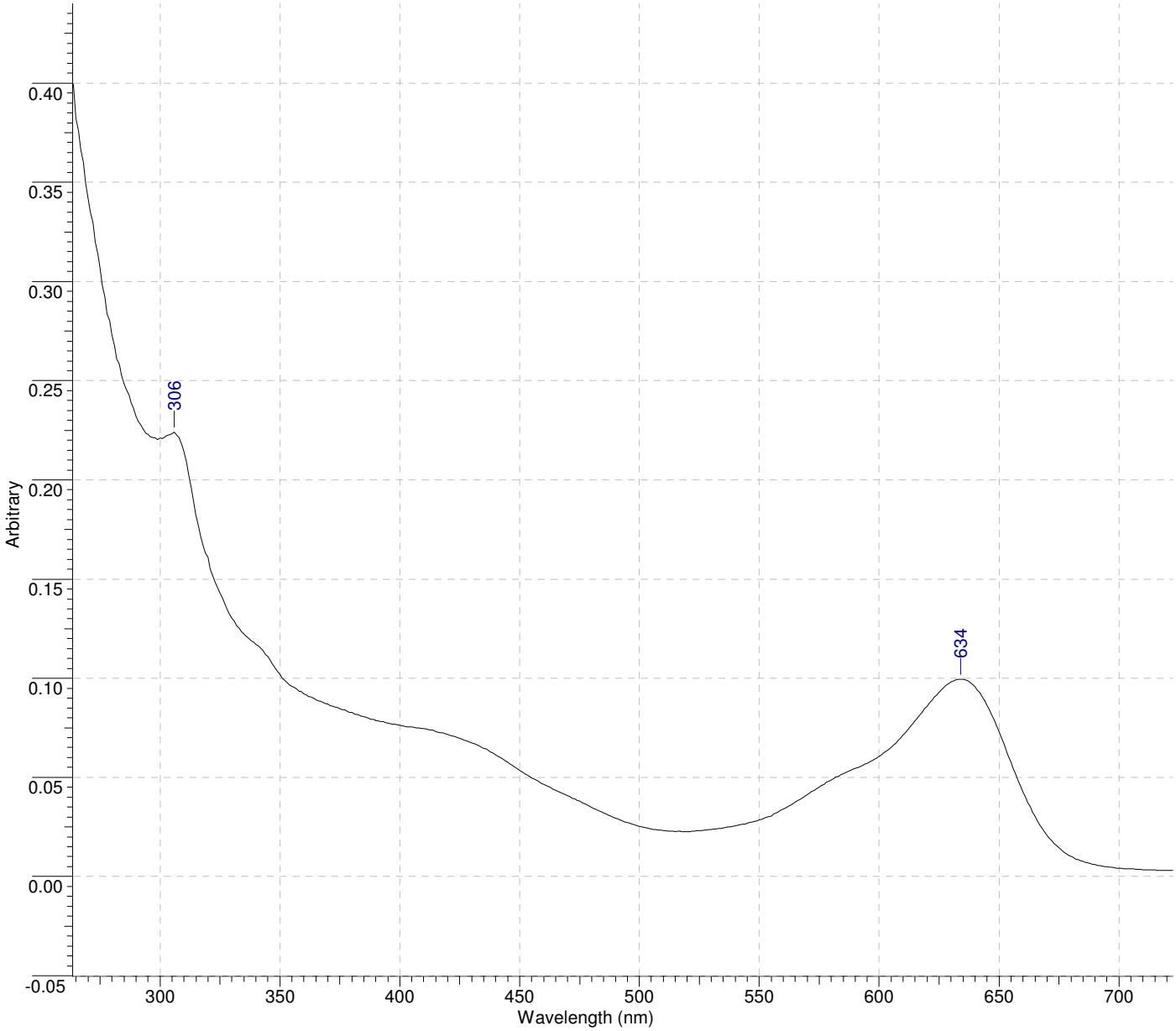
0.20 mmol (0.162 g) **22** have been converted and purified according to general procedure C yielding 0.135 g (83%) **25** as a red solid. R_f=0.10/0.30 (SiO_2, DCM); m.p. Cr 198.0 °C (50.3 kJ/mol) I (EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=8.23 (s, 2H; 7-H), 7.75 (d, ^3J=7.9 Hz, 2H; 4-H), 7.20 (dd, ^3J=7.8 Hz, ^4J=1.1 Hz, 2H; 5-H), 7.16 (d, ^3J=8.3 Hz, 2H; 6´-H), 6.81 (s, 2H; 3´-H), 6.79 (dd, ^3J=8.5 Hz, ^4J=2.3 Hz, 2H; 5´-H), 3.98 (t, ^3J=6.5 Hz, 4H; α-CH_2), 2.56 (s, 6H; $NCOCH_3$), 2.29 (s, 6H; 2´-CH_3), 1.79 (m, 4H; β-CH_2), 1.46 (m, 4H; γ-CH_2), 1.38-1.18 (m, 32H; CH_2), 0.87 ppm (t, ^3J=6.5 Hz,

6H; alkyl-CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ=183.62 (s; C-3), 170.02 (s; N*C*OCH_3), 159.17 (s; C-4´), 151.31 (s; C-6), 149.16 (s; C-7a), 136.62 (s; C-2´), 132.96 (s; C-1´), 130.67 (d; C-6´), 126.79 (s; C-2), 126.64 (d; C-5), 123.81 (d; C-4), 120.14 (s; C-3a), 118.01 (d; C-7), 116.70 (d; C-3´), 111.91 (d; C-5´), 68.01 (t; α-CH_2), 31.90, 29.59, 29.38, 29.33 (4 × t; CH_2), 29.26 (t; β-CH_2), 26.04 (t; γ-CH_2), 23.98 (q; NCO*C*H_3), 22.67 (t; CH_2), 20.82 (q; C-2´-*C*H_3), 14.10 ppm (q; alkyl-CH_3); IR (ATR): $\tilde{\nu}$=2920 (s), 2850 (s), 1701 (s), 1600 (s), 1507 (w), 1467 (m), 1425 (m), 1363 (m), 1320 (m), 1286 (m), 1234 (s), 1196 (m), 1099 (s), 1066 (w), 970 (w), 903 (w), 863 (w), 840 (w), 813 (w), 780 (w), 743 (w), 723 (w), 700 cm^{-1} (w); UV/Vis ($CHCl_3$, 10 mg/L) λ_{max}: 281 (s), 393 nm (s); elemental analysis calcd (%) for $C_{58}H_{74}N_2O_6$: C 77.82, H 8.33, N 3.13, found: C 77.86, H 8.30, N 3.08.

PO12-4,4´-Indi (8)

1 Aug 2008

File Name	G:\JAPO2\INDIGO IN NMP.CSV			***Date***	19 Mar 2007 20:16:46
Technique	UV-Visible	***Spectral Region***	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)
Y Axis	Arbitrary	***Spectrum Range***	200.0000 - 800.0000		
Points Count	601	***Data Spacing***	1.0000		

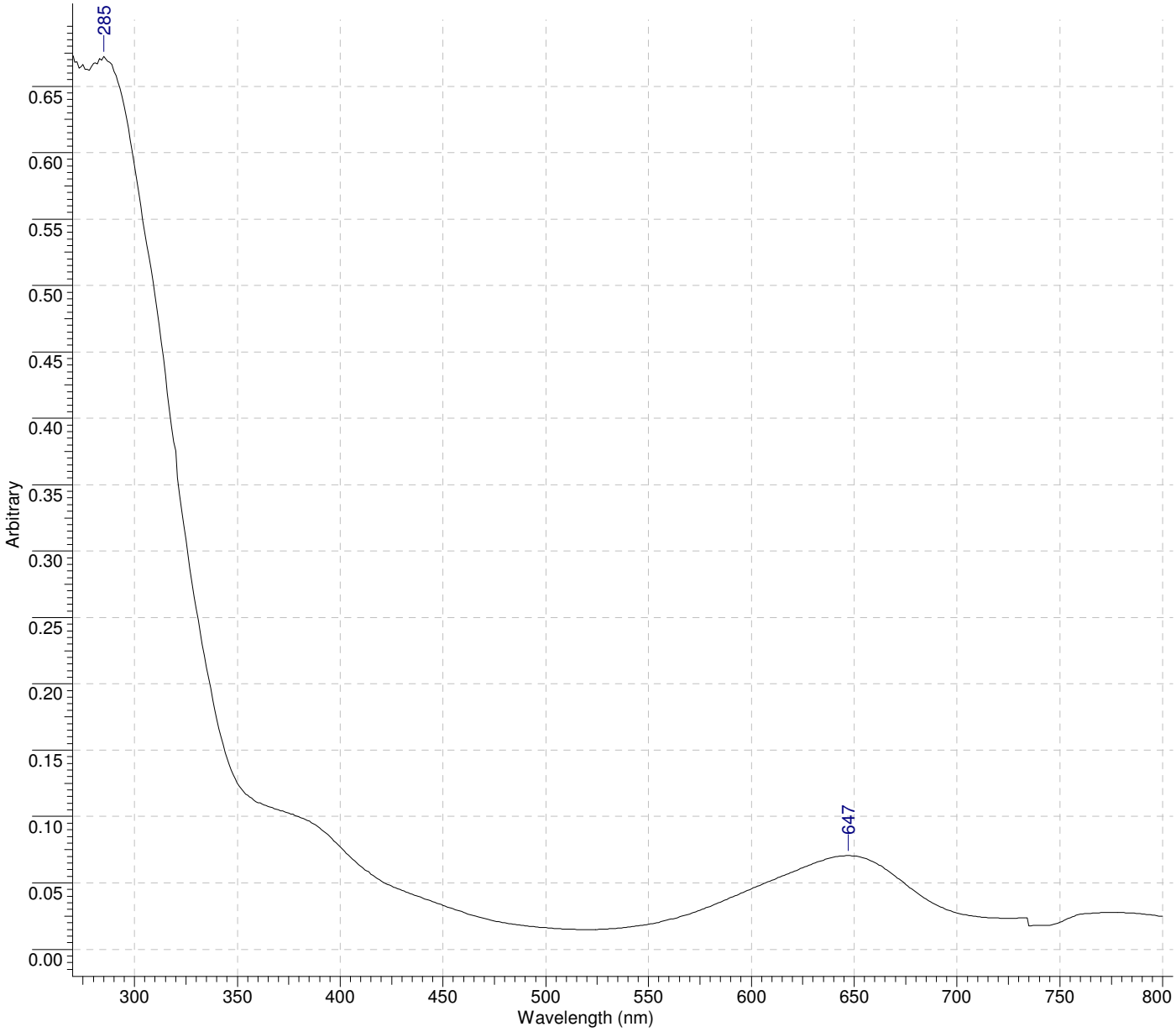


No	nm	Arbitrary	Intensity
1	306.00	0.224	W
2	634.00	0.100	VW

PO12-5,5´-Indi (9)

1 Aug 2008

File Name	G:\JAPO2\INDIGO IN NMP.CSV			***Date***	19 Mar 2007 20:16:46
Technique	UV-Visible	***Spectral Region***	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)
Y Axis	Arbitrary	***Spectrum Range***	200.0000 - 800.0000		
Points Count	601	***Data Spacing***	1.0000		

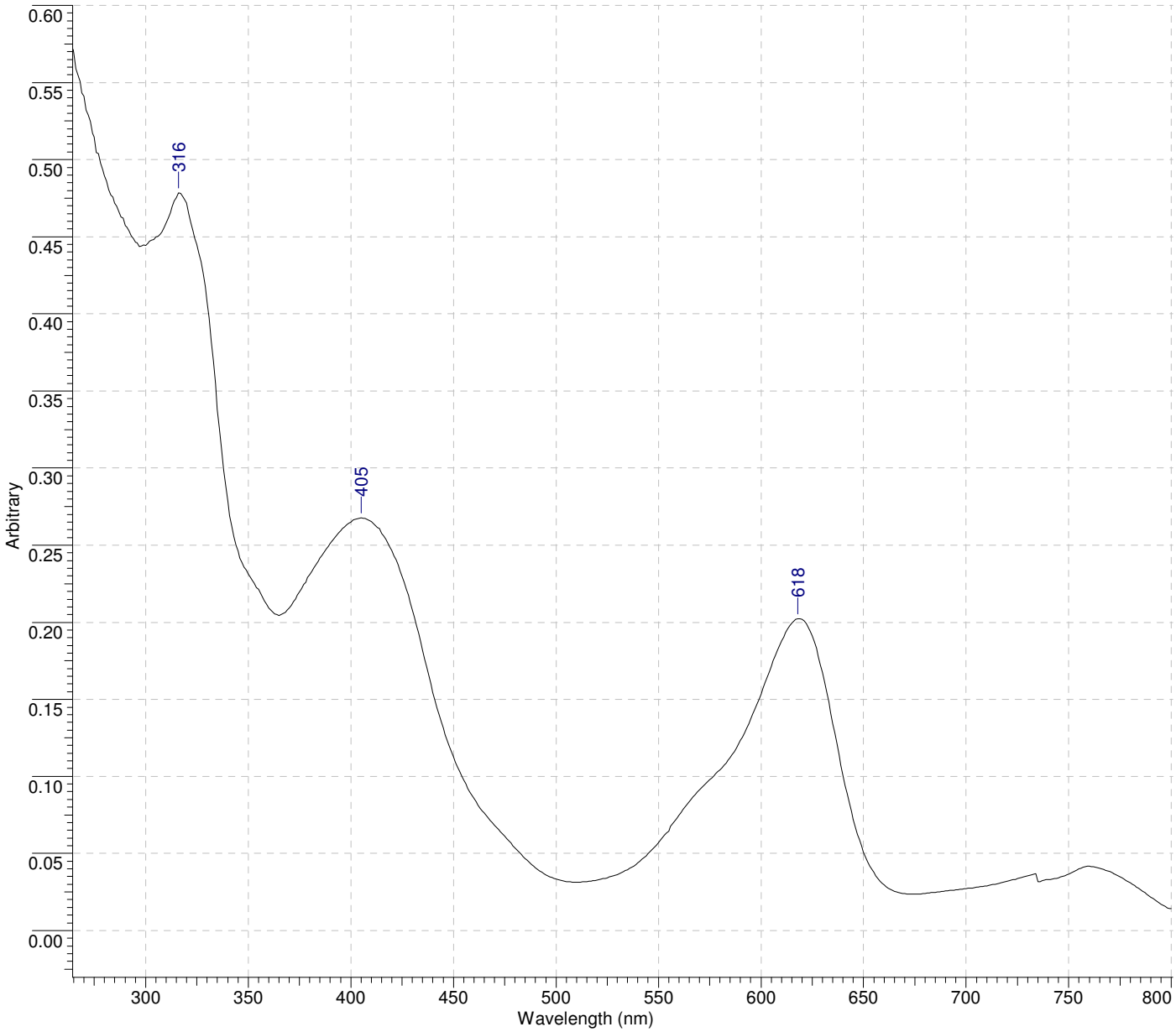


No	nm	Arbitrary	FWHH	Asym	Intensity
1	285.00	0.672	72.82	0.06	W
2	647.00	0.071	103.17	-0.54	VW

PO12-6,6´-Indi (10)

1 Aug 2008

File Name	G:\JAPO2\INDIGO IN NMP.CSV			***Date***	19 Mar 2007 20:16:46
Technique	UV-Visible	***Spectral Region***	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)
Y Axis	Arbitrary	***Spectrum Range***	200.0000 - 800.0000		
Points Count	601	***Data Spacing***	1.0000		

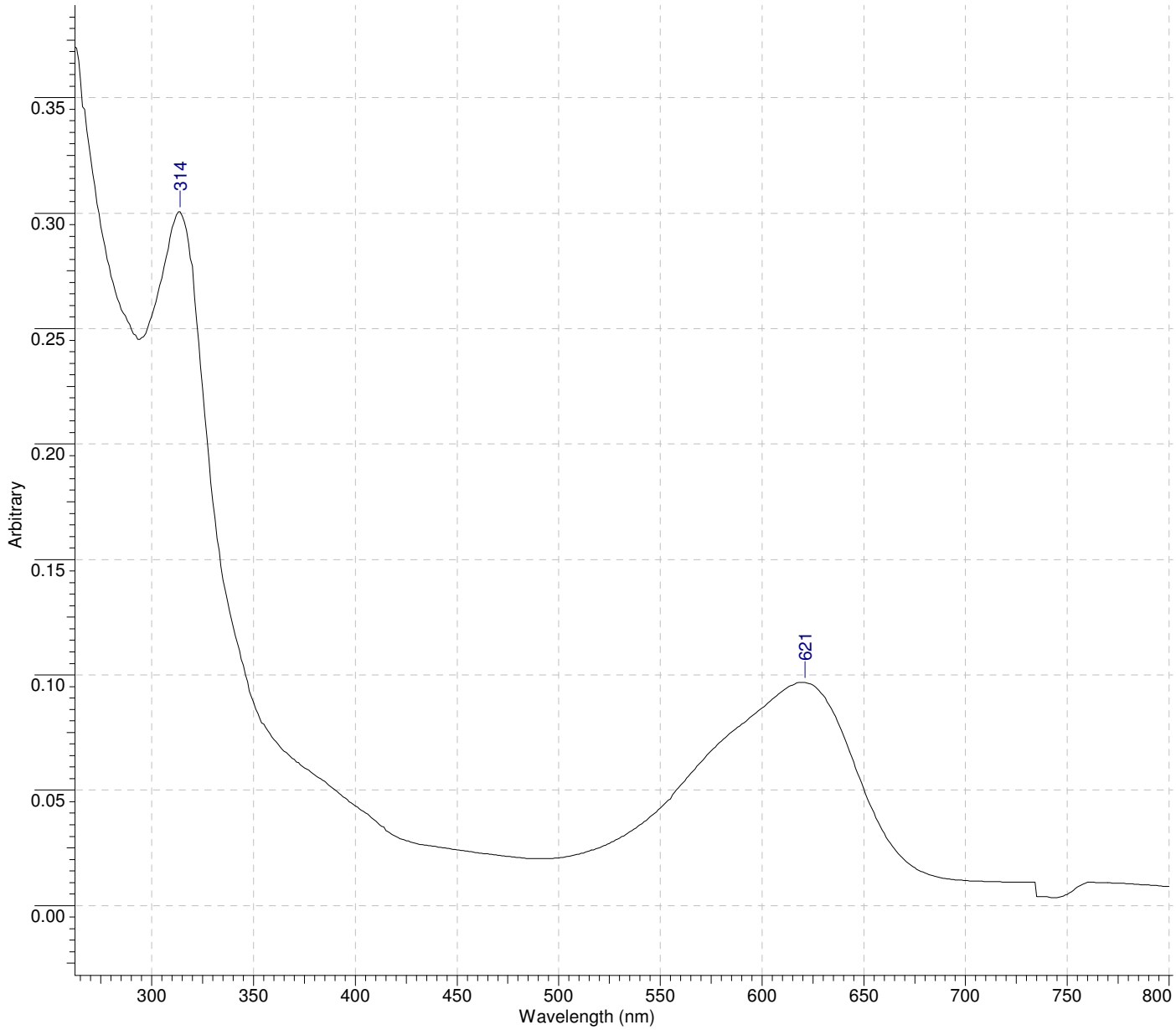


No	nm	Arbitrary	Intensity
1	316.00	0.479	W
2	405.00	0.268	W
3	618.00	0.202	W

PO12-7,7´-Indi (11)

1 Aug 2008

File Name	G:\JAPO2\INDIGO IN NMP.CSV			***Date***	19 Mar 2007 20:16:46
Technique	UV-Visible	***Spectral Region***	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)
Y Axis	Arbitrary	***Spectrum Range***	200.0000 - 800.0000		
Points Count	601	***Data Spacing***	1.0000		

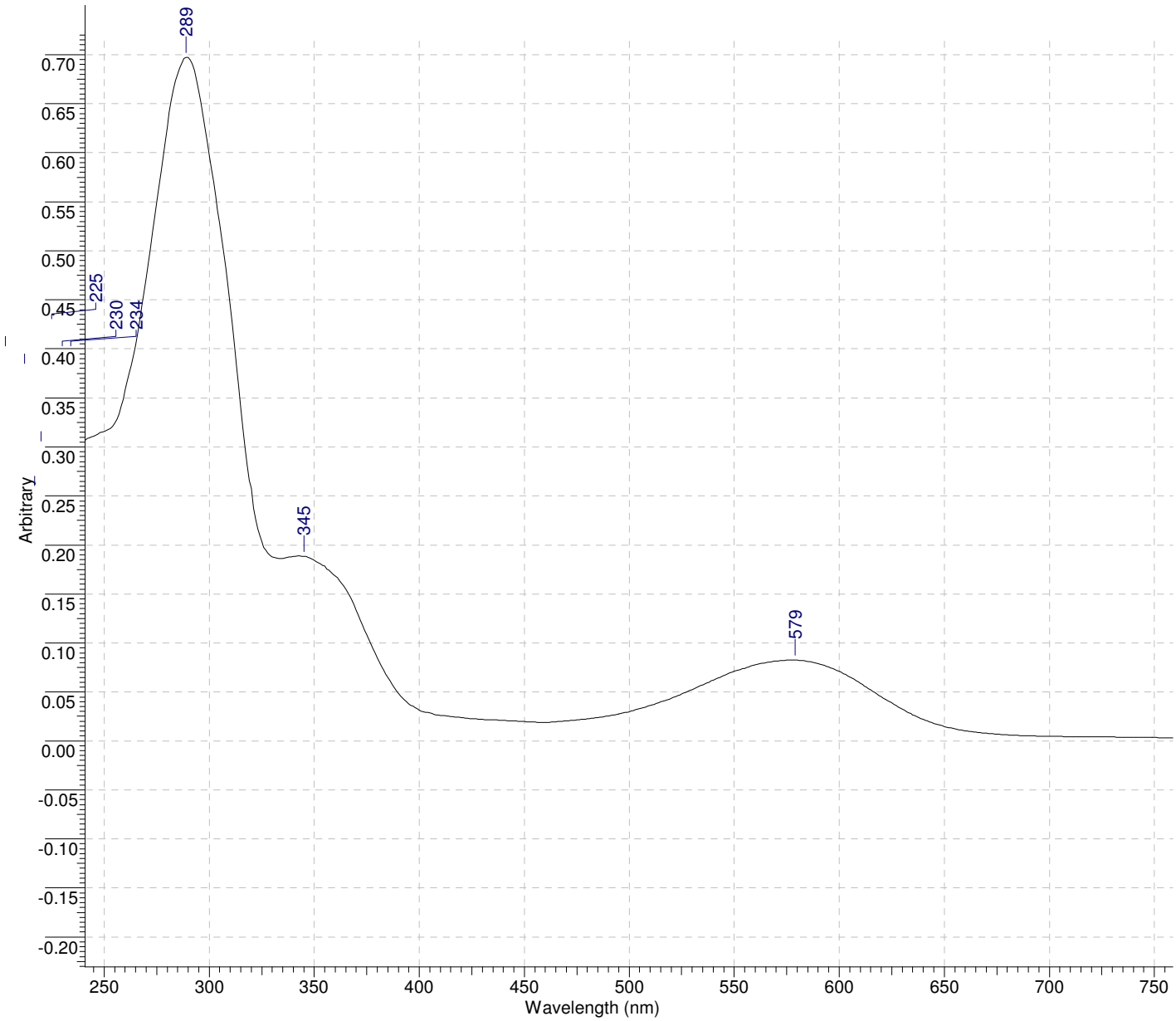


No	nm	Arbitrary	Intensity
1	314.00	0.301	W
2	621.00	0.097	VW

PO12-5,5´-Indi-N,N´-Ac (12)

1 Aug 2008

File Name	G:\JAPO\ACETYLIERTEINDIGOS.CSV			***Date***	18 Mar 2007 20:30:52
Technique	UV-Visible	***Spectral Region***	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)
Y Axis	Arbitrary	***Spectrum Range***	200.0000 - 800.0000		
Points Count	601	***Data Spacing***	1.0000		

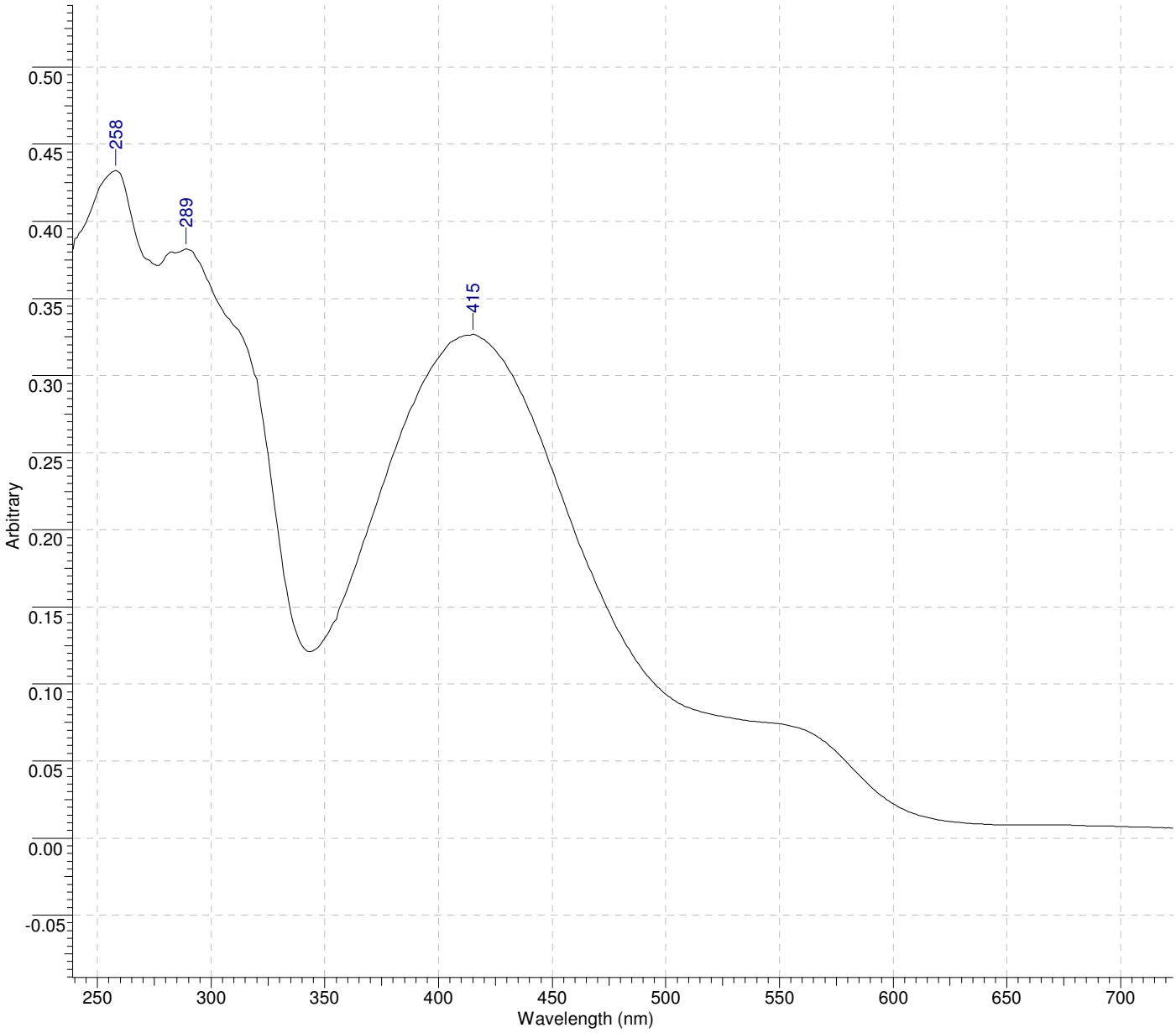


No	nm	Arbitrary	FWHH	Asym	Intensity
1	203.00	0.398	0.71	-0.15	S
2	212.00	0.380	-	-	S
3	217.00	0.255	1.04	-0.63	M
4	220.00	0.301	-	-	M
5	225.00	0.426	1.99	-0.61	S
6	230.00	0.398	-	-	S
7	234.00	0.398	-	-	S
8	289.00	0.697	55.59	-0.17	VS
9	345.00	0.188	-	-	M
10	579.00	0.083	105.63	-0.41	M

PO12-6,6´-Indi-N,N´-Ac (13)

1 Aug 2008

File Name	G:\JAPO\ACETYLIERTEINDIGOS.CSV			***Date***	18 Mar 2007 20:30:52
Technique	UV-Visible	***Spectral Region***	UV-Vis-NIR	***X Axis***	Wavelength (nanometers)
Y Axis	Arbitrary	***Spectrum Range***	200.0000 - 800.0000		
Points Count	601	***Data Spacing***	1.0000		



No	nm	Arbitrary	FWHH	Asym	Intensity
1	258.00	0.433	-	-	S
2	289.00	0.382	-	-	S
3	415.00	0.327	109.55	-0.00	S

Calculation of the Order Parameter S:

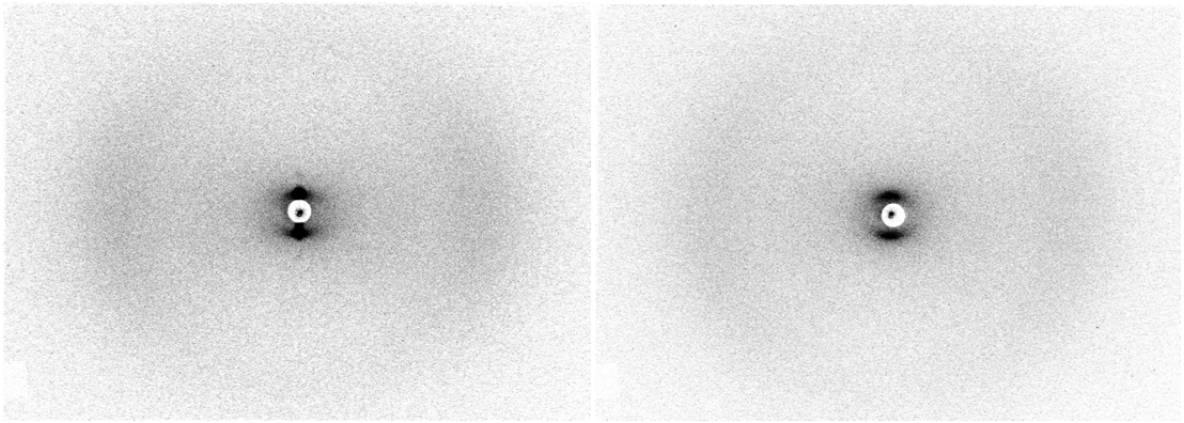


Figure 1: Wide angle diffractogram of the LC phases of **24**. Left: SmA-phase at 144 °C (irradiation: 20 min, cooled from 148 °C with 0.2 K/min), right: N-phase at 148 °C (irradiation: 15 min, cooled from 155 °C with 0.2 K/min).

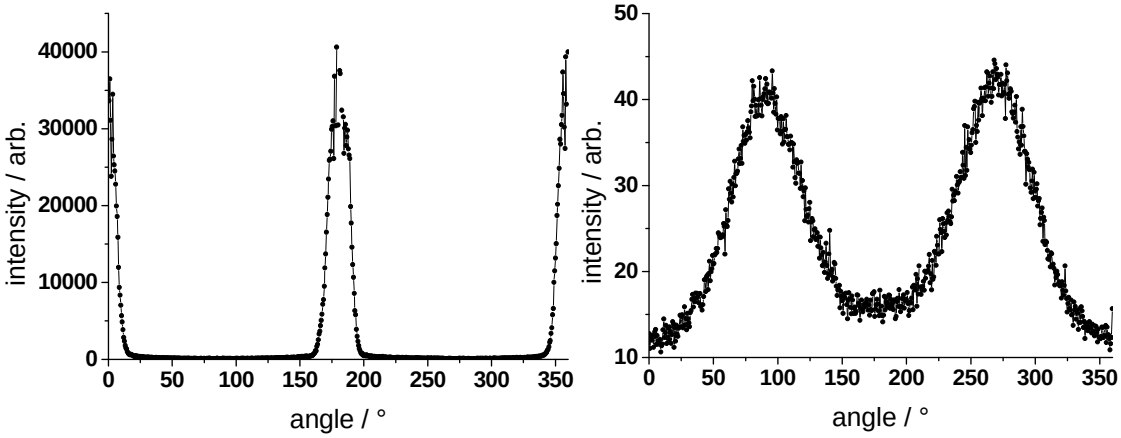


Figure 2: Integration of circular sectors of the diffractogram in Figure 1 left (SmA-phase of **24**) in the small angle area (left) and in the wide angle area (right).

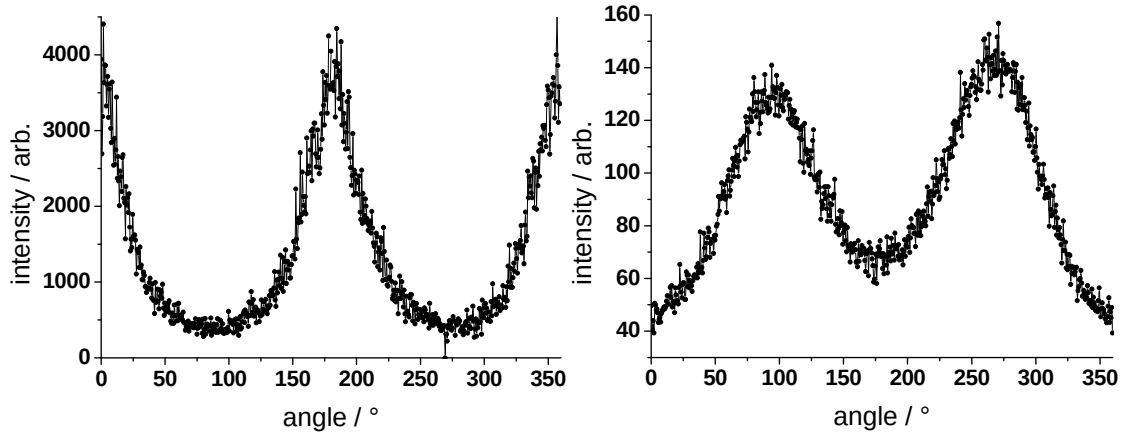


Figure 3: Integration of circular sectors of the diffractogram in Figure 1 right (N-phase of **24**) in the small angle area (left) and in the wide angle area (right).

The order parameter S was calculated from the wide angle diffractograms according to the method of Davidson *et al*.[2] Both sides of each wide angle diffractogram (**Figure 2**, right and **Figure 3**, right) were added and the minimum value was set to zero. (**Figure 4**). The intensity profile I(χ) was fitted to equation 1.

$$I(\chi) = \sum_{n=0}^{\infty} \frac{f_{2n} 2^n n!}{(2n+1)!!} \cos^{2n}(\chi) = f_0 + \frac{2}{3} f_2 \cos^2 \chi + \frac{8}{15} f_4 \cos^4 \chi + \frac{16}{35} f_6 \cos^6 \chi + \ldots \qquad (1)$$

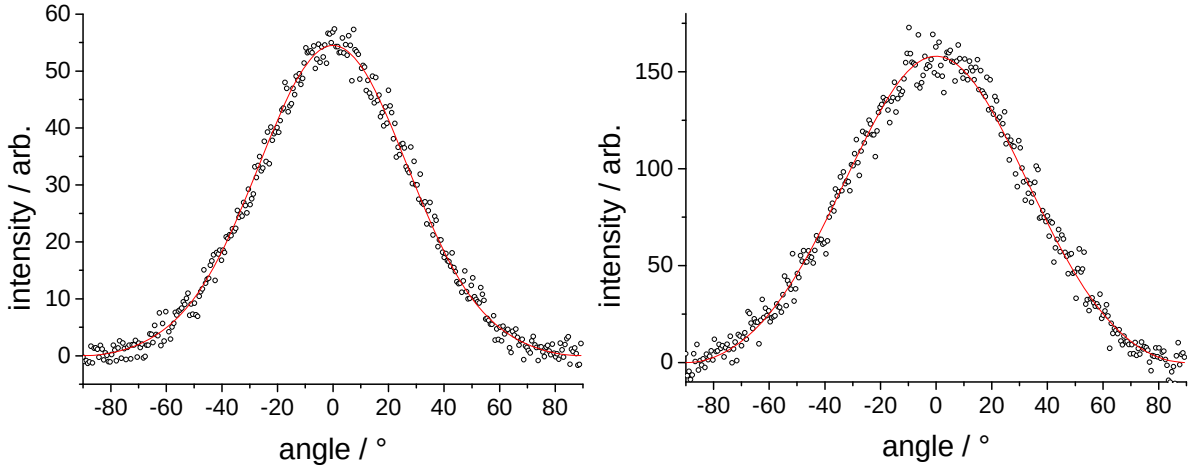


Figure 4: Averaged intensity profile I(χ) from the wide angle reflexes of the LC phases of **24** (left: SmA phase, right N-phase) each with the fit graph of function 1.

Table 1: Fit parameters f_{2n} of the LC phases of **24** and the calculated orderparameters S.

	f_0	f_2	f_4	f_6	S
SmA (144 °C)	0.00443	23.3065	17.30246	65.0806	0.54956
N (148 °C)	0.01574	132.12652	83.47749	55.55415	0.47239

The received fit parameters f_{2n} (**Table 1**) were introduced in the Legendre-polynome (2) of the distribution function and the order parameter was calculated according to equation 3.

$$\left\langle \cos^2 \theta \right\rangle = \frac{\sum_{n=0}^{\infty} \frac{1}{2n+3} f_{2n}}{\sum_{n=0}^{\infty} \frac{1}{2n+1} f_{2n}} = \frac{\frac{1}{3} f_0 + \frac{1}{5} f_2 + \frac{1}{7} f_4 + \frac{1}{9} f_6 + \ldots}{f_0 + \frac{1}{3} f_2 + \frac{1}{5} f_4 + \frac{1}{7} f_6 + \ldots} \qquad (2)$$

$$S = \frac{1}{2}\left(3\left\langle \cos^2 \theta \right\rangle - 1\right) \qquad (3)$$

Quantum mechanical Calculations (DFT):

The geometies and energies of all compounds were computed in Gaussian 03[3] on a DFT level of theory with the B3LYP density functional[4] and the 6-311G(d) basis set. The energetic and atomic parameters are summarized in **Table 3** (*N,N'*-diacetyl indigo in the „twisted"C_2-symmetric conformation), **Table 4** (*N,N'*-diacetyl indigo in the "stepped" C_i-symmetric conformation), **Table 5** (5,5'-bis-(4-ethylphenyl)-*N,N*'-diacetyl indigo in C_2-symmetry), **Table 6** (5,5'-bis-(4-methoxyphenyl)-*N,N*'-diacetyl indigo in C_2-symmetry), **Table 7** (6,6'-bis-(4-ethylphenyl)-*N,N*'-diacetyl indigo in C_2-symmetry) and **Table 8** (6,6'-bis-(4-methoxyphenyl)-*N,N*'-diacetyl indigo in C_2-symmetry).

The energetic difference ΔH was for the total energy and the sum of electronic and zero-point Energies and are presented in **Table 2**. A conversion factor of 2625.50 was used to conver Hartree into kJ/mol.

Table 2: Energy differences between the C_2 and the C_i symmetric conformer of *N,N'*-diacetyl indigo.

	C_2	C_i	ΔH [Hartree]	ΔH [kJ/mol]
Total energy	-1181,24424516	-1181,23155204	0.01269312	33.326
sum of electronic and ZP energies	-1180,944413	-1180,932185	0.012228	32.105

Table 3: Summery of the energetic and atomic parameters of the C_2-symmetric conformation of *N,N'*-diacetyl indigo (DAIndigo_C2_1_freq.log).

E(RB+HF-LYP) =	-1181,24424516
Sum of electronic and zero-point Energies=	-1180,944413
Sum of electronic and thermal Energies=	-1180,923197
Sum of electronic and thermal Enthalpies=	-1180,922253
Sum of electronic and thermal Free Energies=	-1180,993651
Zero-point correction=	0,299832
(Hartree/Particle)	
Thermal correction to Energy=	0,321048
Thermal correction to Enthalpy=	0,321993
Thermal correction to Gibbs Free Energy=	0,250594
Entropy (cal/mol) =	150,271

Number of imaginary frequencies = 0

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.109957	-2.614190	-0.573133
2	6	0	1.920071	-3.590623	-1.146446
3	6	0	1.358357	-4.829331	-1.429838
4	6	0	0.011547	-5.067269	-1.130846
5	6	0	-0.809125	-4.098064	-0.549640
6	6	0	-0.236042	-2.859615	-0.271307
7	1	0	2.958981	-3.367539	-1.363714
8	1	0	-1.847008	-4.294311	-0.333672

9	6	0	0.143633	-0.666597	0.311164	C2’
10	8	0	-2.517643	0.671681	-0.260808	
11	6	0	-1.452080	1.250114	-0.163681	C3
12	6	0	-1.109957	2.614190	-0.573133	
13	6	0	-0.143633	0.666597	0.311164	C2
14	6	0	0.236042	2.859615	-0.271307	
15	6	0	-1.920071	3.590623	-1.146446	
16	7	0	0.809125	1.702095	0.338848	N
17	6	0	0.809125	4.098064	-0.549640	
18	6	0	-1.358357	4.829331	-1.429838	
19	1	0	-2.958981	3.367539	-1.363714	
20	6	0	-0.011547	5.067269	-1.130846	
21	1	0	1.847008	4.294311	-0.333672	
22	6	0	1.452080	-1.250114	-0.163681	
23	8	0	2.517643	-0.671681	-0.260808	
24	7	0	-0.809125	-1.702095	0.338848	
25	6	0	-2.020257	-1.771969	1.083580	
26	6	0	-2.225046	-0.811815	2.232174	
27	1	0	-1.378164	-0.164164	2.448246	
28	1	0	-3.098576	-0.196457	2.021626	
29	1	0	-2.445726	-1.419852	3.111886	
30	8	0	-2.806665	-2.661425	0.863542	
31	6	0	2.020257	1.771969	1.083580	
32	6	0	2.225046	0.811815	2.232174	
33	1	0	3.098576	0.196457	2.021626	
34	1	0	2.445726	1.419852	3.111886	
35	1	0	1.378164	0.164164	2.448246	
36	8	0	2.806665	2.661425	0.863542	
37	1	0	-0.419193	-6.036169	-1.362007	
38	1	0	0.419193	6.036169	-1.362007	
39	1	0	-1.956061	5.609349	-1.888336	
40	1	0	1.956061	-5.609349	-1.888336	

Table 4: Summery of the energetic and atomic parameters of the C_i-symmetric conformation of *N,N‘*-diacetyl indigo (DAIndigo_Ci_1_freq.log).

E(RB+HF-LYP) =	-1181,23155204
Sum of electronic and zero-point Energies=	-1180,932185
Sum of electronic and thermal Energies=	-1180,910990
Sum of electronic and thermal Enthalpies=	-1180,910046
Sum of electronic and thermal Free Energies=	-1180,982144
Zero-point correction=	0,299367
(Hartree/Particle)	
Thermal correction to Energy=	0,320562
Thermal correction to Enthalpy=	0,321506
Thermal correction to Gibbs Free Energy=	0,249408
Entropy (cal/mol) =	151,743
Number of imaginary frequencies = 0	
Standard orientation:	

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.814303	0.302780	2.878817
2	6	0	0.823127	0.304681	4.271626
3	6	0	2.050558	0.302983	4.922471
4	6	0	3.235301	0.305755	4.174862
5	6	0	3.238613	0.310862	2.778725
6	6	0	2.002776	0.312590	2.137948
7	1	0	-0.114853	0.304679	4.816436

8	1	0	4.159306	0.307475	2.215242
9	6	0	0.317726	0.174769	0.576530
10	8	0	1.504282	-0.338384	-2.194153
11	6	0	0.314246	-0.287949	-1.947783
12	6	0	-0.814303	-0.302780	-2.878817
13	6	0	-0.317726	-0.174769	-0.576530
14	6	0	-2.002776	-0.312590	-2.137948
15	6	0	-0.823127	-0.304681	-4.271626
16	7	0	-1.707713	-0.369173	-0.743415
17	6	0	-3.238613	-0.310862	-2.778725
18	6	0	-2.050558	-0.302983	-4.922471
19	1	0	0.114853	-0.304679	-4.816436
20	6	0	-3.235301	-0.305755	-4.174862
21	1	0	-4.159306	-0.307475	-2.215242
22	6	0	-0.314246	0.287949	1.947783
23	8	0	-1.504282	0.338384	2.194153
24	7	0	1.707713	0.369173	0.743415
25	6	0	2.632274	1.046698	-0.124555
26	8	0	3.812993	0.850952	0.006724
27	6	0	-2.632274	-1.046698	0.124555
28	6	0	-2.094930	-2.137139	1.020877
29	1	0	-2.467434	-1.985742	2.032531
30	1	0	-2.508396	-3.077947	0.646045
31	1	0	-1.010144	-2.218488	1.038140
32	8	0	-3.812993	-0.850952	-0.006724
33	1	0	2.508396	3.077947	-0.646045
34	6	0	2.094930	2.137139	-1.020877
35	1	0	1.010144	2.218488	-1.038140
36	1	0	2.467434	1.985742	-2.032531
37	1	0	-4.188599	-0.297984	-4.693636
38	1	0	4.188599	0.297984	4.693636
39	1	0	2.096116	0.293307	6.005719
40	1	0	-2.096116	-0.293307	-6.005719

Table 5: Summery of the energetic and atomic parameters of the C_2-symmetric conformation of 5,5'-bis-(4-ethylphenyl)-*N,N*'-diacetyl indigo (55-DiPhEt-DAIndigo).

E(RB3LYP)=	-1800.74272629
Sum of electronic and zero-point Energies=	-1800.169811
Sum of electronic and thermal Energies=	-1800.132775
Sum of electronic and thermal Enthalpies=	-1800.131830
Sum of electronic and thermal Free Energies=	-1800.242324
Zero-point correction=	0.572915
(Hartree/Particle)	
Thermal correction to Energy=	0.609952
Thermal correction to Enthalpy=	0.610896
Thermal correction to Gibbs Free Energy=	0.500402
Entropy (cal/mol) =	232.554

Number of imaginary frequencies = 0

Standard orientation:

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000011052	-0.000000713	-0.000017728
2	6	0.000002173	0.000000143	-0.000009015
3	6	-0.000011692	0.000001013	0.000008337
4	6	0.000004588	-0.000002276	0.000002010
5	6	0.000004703	0.000003661	-0.000000522
6	6	0.000001474	0.000000178	0.000003005
7	1	0.000003088	-0.000000011	0.000000059

8	1	0.000001718	-0.000003626	-0.000002980
9	6	-0.000008801	0.000005340	-0.000021388
10	8	-0.000002301	0.000006028	0.000009357
11	6	0.000009096	-0.000003646	-0.000021802
12	6	-0.000001782	0.000002437	0.000009180
13	6	-0.000005384	0.000001542	0.000016288
14	6	0.000000537	-0.000000878	-0.000000328
15	6	-0.000004745	0.000000806	-0.000002107
16	7	-0.000004180	-0.000001793	0.000007988
17	6	-0.000002809	-0.000002535	-0.000000414
18	6	0.000011080	-0.000000093	0.000005347
19	1	-0.000001803	-0.000000381	-0.000000280
20	6	-0.000001707	0.000000581	0.000000143
21	1	-0.000000312	0.000001268	-0.000001124
22	6	0.000027236	-0.000011095	0.000060499
23	8	-0.000011097	0.000007658	-0.000019799
24	7	-0.000000878	-0.000004979	0.000005983
25	6	0.000004257	-0.000000808	0.000001145
26	6	-0.000001944	-0.000002241	-0.000009024
27	1	-0.000001473	-0.000003498	-0.000002934
28	1	0.000001106	0.000001945	-0.000000666
29	1	0.000001602	-0.000002094	0.000002246
30	8	-0.000013497	0.000009064	0.000003684
31	6	0.000031152	-0.000011591	-0.000029204
32	6	-0.000008614	0.000007307	-0.000001945
33	1	-0.000003386	-0.000001663	-0.000003123
34	1	-0.000000532	0.000002365	0.000004396
35	1	0.000001257	0.000004262	-0.000001383
36	8	-0.000006051	-0.000001477	0.000013788
37	1	0.000000783	-0.000000034	-0.000002374
38	1	-0.000000440	0.000000010	-0.000000259
39	6	-0.000009907	-0.000020282	-0.000017108
40	6	-0.000020184	0.000023886	0.000001508
41	6	0.000017997	-0.000000531	0.000008989
42	6	0.000031101	-0.000005128	0.000019841
43	1	0.000001647	-0.000003006	-0.000001008
44	6	-0.000003336	0.000017465	0.000010623
45	1	-0.000002745	-0.000000581	-0.000001568
46	6	-0.000033103	-0.000013499	-0.000028519
47	1	-0.000004096	0.000001298	-0.000000241
48	1	0.000001988	-0.000005288	-0.000003167
49	6	0.000011497	0.000021431	-0.000019618
50	6	-0.000021132	0.000000180	0.000009342
51	6	0.000019917	-0.000024937	0.000002545
52	6	0.000005868	-0.000018828	0.000012024
53	1	0.000001706	0.000001263	0.000000225
54	6	-0.000031106	0.000003441	0.000019800
55	1	-0.000002956	0.000003067	-0.000001047
56	6	0.000034869	0.000017453	-0.000029455
57	1	-0.000002173	0.000004726	-0.000003583
58	1	0.000004153	-0.000001677	-0.000000603
59	6	-0.000015697	0.000018584	0.000037024
60	6	-0.000019511	-0.000011861	-0.000017598
61	1	0.000005431	-0.000008176	-0.000006707
62	1	0.000006385	0.000000751	-0.000012151
63	1	0.000003337	-0.000001590	-0.000003840
64	1	0.000001019	0.000000255	0.000010425
65	1	0.000001898	0.000009930	0.000001050
66	6	0.000014812	-0.000019202	0.000036292
67	6	0.000019340	0.000012035	-0.000017781
68	1	-0.000005953	0.000008021	-0.000006935
69	1	-0.000005928	-0.000000324	-0.000011328

70	1	-0.000003497	0.000001469	-0.000003698
71	1	-0.000001035	-0.000000364	0.000010021
72	1	-0.000001975	-0.000010155	0.000001193

Table 6: Summery of the energetic and atomic parameters of the C_2-symmetric conformation of 5,5'-bis-(4-methoxyphenyl)-*N,N*'-diacetyl indigo (55-DiPhOMe-DAIndigo)

E(RB3LYP)=	-1872.55162178
Sum of electronic and zero-point Energies=	-1872.025987
Sum of electronic and thermal Energies=	-1871.989817
Sum of electronic and thermal Enthalpies=	-1871.988873
Sum of electronic and thermal Free Energies=	-1872.096538
Zero-point correction=	0.525635
(Hartree/Particle)	
Thermal correction to Energy=	0.561805
Thermal correction to Enthalpy=	0.562749
Thermal correction to Gibbs Free Energy=	0.455083
Entropy (cal/mol)=	226.601

Number of imaginary frequencies = 0

Standard orientation:

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000003709	0.000005058	-0.000000264
2	6	-0.000002477	-0.000001745	-0.000002358
3	6	-0.000001041	0.000003899	0.000000754
4	6	0.000000317	0.000000798	-0.000000261
5	6	-0.000003743	-0.000002295	0.000003352
6	6	-0.000001007	0.000004348	-0.000002665
7	1	0.000000908	0.000000533	0.000000899
8	1	0.000000062	0.000002187	0.000000090
9	6	0.000011293	0.000001409	0.000003719
10	8	-0.000001446	-0.000006371	-0.000001364
11	6	0.000004889	0.000007375	0.000002312
12	6	-0.000004671	-0.000005132	-0.000002233
13	6	-0.000006391	0.000004173	-0.000005056
14	6	0.000004359	-0.000001789	-0.000000178
15	6	0.000002833	0.000001314	-0.000000320
16	7	-0.000004171	0.000001995	0.000001813
17	6	0.000001347	0.000001006	0.000001308
18	6	0.000000097	-0.000003829	-0.000000722
19	1	-0.000000954	-0.000000842	0.000000554
20	6	0.000000183	-0.000000882	0.000000773
21	1	0.000001255	-0.000002552	0.000000337
22	6	-0.000006151	-0.000001182	-0.000003073
23	8	0.000004364	-0.000000118	-0.000002759
24	7	-0.000001634	-0.000010177	0.000007235
25	6	-0.000007676	0.000018713	-0.000009529
26	6	0.000003025	-0.000003032	0.000003116
27	1	0.000000179	-0.000000097	-0.000000328
28	1	-0.000000931	-0.000000418	0.000000255
29	1	-0.000001797	0.000000034	0.000000308
30	8	0.000002989	-0.000009176	0.000001358
31	6	-0.000002976	-0.000008356	0.000001649
32	6	0.000002248	0.000002272	0.000001923
33	1	0.000000024	-0.000000566	0.000001073
34	1	0.000000638	-0.000000650	-0.000000366
35	1	-0.000000406	0.000000008	-0.000000325
36	8	0.000001292	0.000004494	-0.000002149
37	1	0.000000083	0.000001117	0.000000193

38	1	0.000000171	-0.000001457	0.000000346
39	6	-0.000002015	-0.000005615	-0.000002939
40	6	-0.000000327	0.000004146	0.000001545
41	6	0.000006282	-0.000000613	0.000001943
42	6	0.000006280	-0.000003094	0.000002261
43	1	0.000000059	-0.000002016	0.000000246
44	6	-0.000005338	0.000006509	0.000000087
45	1	-0.000000085	-0.000002705	0.000000296
46	6	0.000001544	-0.000011412	0.000003642
47	1	-0.000001787	-0.000002219	-0.000001212
48	1	0.000001952	-0.000004283	0.000000573
49	6	0.000003557	0.000001803	-0.000001483
50	6	-0.000005183	0.000002269	-0.000000291
51	6	0.000000320	-0.000001768	0.000003347
52	6	0.000004448	-0.000007794	0.000000715
53	1	0.000000327	0.000002493	0.000000109
54	6	-0.000001474	0.000005594	0.000001063
55	1	-0.000000867	0.000002125	0.000000444
56	6	-0.000002932	0.000005719	-0.000000297
57	1	-0.000001038	0.000005436	0.000000688
58	1	0.000001452	0.000001876	-0.000001108
59	6	-0.000001658	0.000007900	-0.000011030
60	1	0.000002746	0.000001815	0.000000453
61	1	0.000001334	0.000002524	0.000002105
62	1	0.000000814	0.000000074	0.000003640
63	6	0.000000023	-0.000006008	-0.000008066
64	1	-0.000002446	-0.000001702	-0.000000646
65	1	-0.000000945	-0.000002708	0.000001906
66	1	-0.000000971	0.000000087	0.000002167
67	8	0.000000604	0.000000043	0.000001950
68	8	-0.000003464	0.000001458	-0.000001524

Table 7: Summery of the energetic and atomic parameters of the C_2-symmetric conformation of 6,6'-bis-(4-ethylphenyl)-*N,N*'-diacetyl indigo (66-DiPhEt-DAIndigo).

E(RB3LYP)=	-1800.74452635
Sum of electronic and zero-point Energies=	-1800.171571
Sum of electronic and thermal Energies=	-1800.134472
Sum of electronic and thermal Enthalpies=	-1800.133527
Sum of electronic and thermal Free Energies=	-1800.244653
Zero-point correction=	0.572955
(Hartree/Particle)	
Thermal correction to Energy=	0.610055
Thermal correction to Enthalpy=	0.610999
Thermal correction to Gibbs Free Energy=	0.499873
Entropy (cal/mol)=	233.885

Number of imaginary frequencies = 0

Standard orientation:

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000009876	-0.000004739	0.000001153
2	6	-0.000004858	0.000000409	0.000002857
3	6	0.000005059	0.000000733	-0.000000527
4	6	-0.000011236	0.000002303	-0.000005564
5	6	0.000003006	-0.000003984	0.000003588
6	6	-0.000002327	0.000002905	-0.000001677
7	1	-0.000000194	-0.000000414	-0.000001598

8	1	0.000001864	0.000001233	0.000000050
9	6	0.000000594	0.000001200	0.000001168
10	8	-0.000004876	0.000003789	-0.000003219
11	6	0.000010468	-0.000005295	0.000006129
12	6	-0.000012275	0.000004026	-0.000003936
13	6	0.000000353	-0.000000817	-0.000000092
14	6	0.000003200	-0.000002570	0.000001064
15	6	0.000005143	-0.000000885	0.000001142
16	7	-0.000000862	0.000008078	-0.000002860
17	6	-0.000001567	0.000004682	0.000003461
18	6	-0.000005176	-0.000000230	-0.000000538
19	1	0.000000390	0.000000488	-0.000001537
20	6	0.000011355	-0.000002204	-0.000004498
21	1	-0.000002173	-0.000000487	-0.000000974
22	6	-0.000005044	0.000007572	-0.000009513
23	8	0.000003898	-0.000005120	0.000007120
24	7	0.000002450	-0.000007327	-0.000005286
25	6	-0.000019158	-0.000004806	0.000019557
26	6	0.000004415	0.000005481	-0.000000786
27	1	-0.000000911	-0.000000387	-0.000001051
28	1	0.000002054	-0.000000045	0.000002250
29	1	-0.000000639	0.000000610	-0.000002311
30	8	0.000006823	0.000000181	-0.000009062
31	6	0.000003689	-0.000013162	-0.000003325
32	6	0.000000086	0.000002095	-0.000000109
33	1	-0.000001107	-0.000000486	-0.000000596
34	1	-0.000000418	-0.000001259	-0.000001049
35	1	0.000000173	0.000002456	-0.000000857
36	8	-0.000001991	0.000005611	0.000002614
37	1	-0.000002001	0.000002820	0.000001406
38	1	0.000002160	-0.000002851	0.000001414
39	6	-0.000008333	-0.000004317	0.000014964
40	6	-0.000013027	0.000007127	-0.000005408
41	6	0.000014489	0.000002257	-0.000007580
42	6	0.000017687	-0.000000502	-0.000010958
43	1	0.000002706	0.000000317	0.000001039
44	6	-0.000011409	0.000007336	-0.000005974
45	1	-0.000001325	-0.000000341	0.000000508
46	6	-0.000011539	-0.000003774	0.000015447
47	1	-0.000002565	0.000001778	0.000001701
48	1	0.000002490	0.000001016	0.000001790
49	6	0.000007926	0.000004860	0.000016544
50	6	-0.000016142	-0.000002278	-0.000008761
51	6	0.000014447	-0.000007863	-0.000005654
52	6	0.000012681	-0.000008627	-0.000006298
53	1	0.000001354	0.000000587	0.000000467
54	6	-0.000018662	0.000000971	-0.000012328
55	1	-0.000002586	-0.000000236	0.000001143
56	6	0.000011914	0.000005314	0.000017986
57	1	-0.000002698	-0.000000990	0.000001745
58	1	0.000002493	-0.000001969	0.000001708
59	6	-0.000015819	0.000005213	-0.000009015
60	6	0.000000971	-0.000003233	0.000000825
61	1	0.000002735	-0.000001271	0.000003839
62	1	0.000005127	-0.000006034	0.000001235
63	1	0.000001160	-0.000004761	0.000000227
64	1	0.000000322	0.000001249	0.000002165
65	1	-0.000001964	0.000000509	-0.000002685
66	6	0.000015585	-0.000005328	-0.000008753
67	6	-0.000001050	0.000003134	0.000001078
68	1	-0.000002711	0.000001610	0.000004122
69	1	-0.000005053	0.000005667	0.000001055

70	1	-0.000001140	0.000004679	0.000000394
71	1	-0.000000418	-0.000001280	0.000002104
72	1	0.000002108	-0.000000421	-0.000002678

Table 8: Summery of the energetic and atomic parameters of the C_2-symmetric conformation of 6,6'-bis-(4-methoxyphenyl)-*N,N*'-diacetyl indigo (66-DiPhOMe-DAIndigo).

E(RB3LYP)=	-1872.55412215
Sum of electronic and zero-point Energies=	-1872.028167
Sum of electronic and thermal Energies=	-1871.992080
Sum of electronic and thermal Enthalpies=	-1871.991136
Sum of electronic and thermal Free Energies=	-1872.098429
Zero-point correction=	0.525956
(Hartree/Particle)	
Thermal correction to Energy=	0.562042
Thermal correction to Enthalpy=	0.562986
Thermal correction to Gibbs Free Energy=	0.455693
Entropy (cal/mol)=	225.817

Number of imaginary frequencies = 0

Standard orientation:

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000002506	0.000002559	-0.000004834
2	6	0.000002009	0.000001894	-0.000003401
3	6	-0.000001561	-0.000007924	0.000000835
4	6	0.000011708	0.000004698	-0.000000762
5	6	0.000000382	-0.000002136	-0.000004165
6	6	-0.000000768	-0.000001461	0.000004110
7	1	0.000000735	-0.000000581	0.000000427
8	1	-0.000003470	-0.000002111	-0.000000935
9	6	-0.000004276	-0.000009318	0.000000334
10	8	0.000003545	-0.000001977	0.000011026
11	6	-0.000010921	0.000000943	-0.000017608
12	6	0.000003240	-0.000001119	0.000002337
13	6	0.000005398	0.000010437	-0.000002524
14	6	-0.000005056	0.000001000	-0.000000774
15	6	-0.000000529	0.000000519	0.000004055
16	7	-0.000000019	0.000000451	0.000000841
17	6	-0.000001258	0.000004915	0.000001178
18	6	0.000002799	0.000001890	0.000000277
19	1	-0.000000693	0.000000432	-0.000001295
20	6	-0.000001483	-0.000003142	-0.000005469
21	1	0.000000778	-0.000000754	0.000002421
22	6	-0.000004307	-0.000004717	0.000019626
23	8	0.000002943	0.000004868	-0.000011030
24	7	0.000001308	0.000008453	0.000000575
25	6	0.000001803	-0.000010058	-0.000003770
26	6	-0.000001116	-0.000002043	-0.000007694
27	1	0.000002431	-0.000000280	0.000004627
28	1	-0.000002213	0.000001476	-0.000001655
29	1	0.000000096	-0.000002194	0.000003050
30	8	0.000000335	0.000005369	0.000002536
31	6	0.000008730	-0.000004039	0.000009200
32	6	-0.000005795	0.000002652	0.000002137
33	1	0.000000886	-0.000001321	0.000000727
34	1	0.000000040	0.000000077	-0.000000090
35	1	0.000001784	-0.000001863	-0.000004443
36	8	-0.000001908	0.000001396	-0.000006449
37	1	-0.000002835	0.000001229	0.000003305

38	1	-0.000000314	0.000000850	-0.000000762
39	6	0.000001783	-0.000006882	0.000015265
40	6	-0.000004977	0.000003979	-0.000003912
41	6	0.000011946	0.000002886	-0.000006145
42	6	0.000001441	-0.000001266	-0.000001111
43	1	-0.000000468	0.000000020	-0.000000080
44	6	-0.000006127	0.000005375	-0.000002247
45	1	-0.000002263	-0.000000268	0.000000294
46	6	0.000005328	-0.000001002	0.000006167
47	1	-0.000000308	0.000001634	-0.000000058
48	1	0.000001662	-0.000001236	0.000002902
49	6	-0.000011572	0.000005065	0.000011604
50	6	-0.000005416	-0.000001325	-0.000011950
51	6	0.000009472	-0.000006552	-0.000004962
52	6	0.000014231	-0.000007111	-0.000003666
53	1	0.000002798	0.000000270	0.000002195
54	6	-0.000008686	0.000000891	-0.000008262
55	1	0.000001372	-0.000001783	0.000000838
56	6	-0.000001787	0.000000959	0.000017857
57	1	-0.000001978	0.000000428	0.000002096
58	1	0.000001047	-0.000002940	0.000001091
59	6	-0.000004554	-0.000001319	0.000002913
60	1	-0.000001338	-0.000000170	-0.000001967
61	1	-0.000000992	0.000001165	-0.000002470
62	1	0.000002583	-0.000000932	-0.000001203
63	6	0.000002816	0.000007964	0.000009737
64	1	0.000002465	-0.000000013	-0.000001788
65	1	-0.000001852	-0.000000168	-0.000004592
66	1	-0.000002511	-0.000000253	-0.000000219
67	8	0.000000488	-0.000001494	-0.000009423
68	8	-0.000004524	0.000005004	-0.000004869

Calculation of the p-Orbital Alignment Vectors:

The p-orbital axis vector (POAV) analysis as introduced by *Haddon*[5] is a powerful tool for the description of pyramidalized atoms with hybridization between sp^2 and sp^3 providing the angle of pyramidalization and the degree of hybridization in terms of sp^n.

The POAV1 is definded to originate in the central atom and to have equal angles ≥ 90° to the vectors of all three surrounding atoms. For a perfect sp^2 hybridized atom this angle is 90°, whereas it is the tetrahedral angle of 109.47 for a perfect sp^3 hybridized atom.

However the POAV1 theory assumes an equal σ-bond hybridisation in C_{3v} symmetry and may lead to significant deviations of the actual hybridization, when the bond angles θ_{ij} to the surrounding atoms substantially differ.[5a] This case is given for the here examined indigoid structures and a more accurate description is obtained from the POAV2 theory, which treats the σ-bond hydridisations individually.[5a]

In order to be able to measure the dihedral angle between two POAVs within a structure dummy atoms were placed along these vectors in an arbitrary distance of 1 Å. The procedure which gave the x, y, z coordinates of this dummy atom, according to POAV1 and POAV2 theory, was implemented into an Excel worksheet and is outlined below examplary for the C2 carbon of the calculated structure of *N,N'*-diacetyl indigo with C_2 symmetry. The x, y and z coordinates of the central atom and the three surrounding atoms were gathered (see table DAIndigo_C2_1_freq.log, atoms 9 (C2'), 11 (C3), 16 (N) and 13 (C2)):

Example:

atom		x	y	z
1	(C2')	0.14363	-0.6666	0.31116
2	(C3)	-1.45208	1.25011	-0.16368
3	(N)	0.80912	1.70209	0.33885
center	(C2)	-0.14363	0.6666	0.31116

By substracting the x_c, y_c, and z_c values of the center form the x_i, y_i and z_i values of the atoms 1, 2 and 3 the center was shifted to the origin and the magnitude $\|\vec{V}_i\|$ of the resulting vectors was calculated according to:

$$\|\vec{V}_i\| = \sqrt{x_i^2 + y_i^2 + z_i^2} \tag{4}$$

Example:

vector (from center)	x	y	z	magnitude
V1	0.28726	-1.3332	0	1.3637964
V2	-1.30845	0.58351	-0.47484	1.5093039
V3	0.95275	1.03549	0.02769	1.4073872

The vectors were normalized by dividing the x_i, y_i and z_i values by the corresponding magnitudes $\|\vec{V}_i\|$ and were written in the following matrix representation:

$$\vec{V}_i = \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} \tag{5}$$

Example:

normalized vectors	V1	V2	V3
x	0.2106326	-0.977565	0
y	-0.866923	0.386609	-0.314609
z	0.6769636	0.735753	0.0196748

The POAV1 is obtained from the following relation:[5c]

$$\overrightarrow{V_\pi} = \frac{(\vec{V}_2 - \vec{V}_1) \times (\vec{V}_3 - \vec{V}_1)}{\|(\vec{V}_2 - \vec{V}_1) \times (\vec{V}_3 - \vec{V}_1)\|} = \frac{\vec{a} \times \vec{b}}{\|\vec{a} \times \vec{b}\|} \tag{6}$$

First $\vec{V}_1$was subtracted from $\vec{V}_2$ or $\vec{V}_3$, giving $\vec{a}$ or $\vec{b}$, respectively. Then the cross product between $\vec{a}$ and $\vec{b}$ was fromed according to:

$$\vec{a} \times \vec{b} = \begin{bmatrix} a_x \\ a_y \\ a_z \end{bmatrix} \times \begin{bmatrix} b_x \\ b_y \\ b_z \end{bmatrix} = \begin{bmatrix} a_y b_z - a_z b_y \\ a_z b_x - a_x b_z \\ a_x b_y - a_y b_x \end{bmatrix} \tag{7}$$

The magnitude of the resulting vector was calculated by:

$$\|\vec{a} \times \vec{b}\| = \sqrt{(a_y b_z - a_z b_y)^2 + (a_z b_x - a_x b_z)^2 + (a_z b_x - a_x b_z)^2} \tag{8}$$

Normalizing by dividing the x_i, y_i and z_i values of the cross product $\vec{a} \times \vec{b}$ by its magnitude$\|\vec{a} \times \vec{b}\|$ directly gave the POAV1.

Example:

	a (V2 - V1)	b (V3 - V1)	a × b	$\overrightarrow{V_\pi}$
x	-1.07756	0.466331	0.565865	0.22198
y	1.36417	1.7133187	-0.12551	-0.0492
z	-0.31461	0.0196748	-2.48235	-0.9738
magnitude	1.76666	1.775757	2.549123	1

The angle $\theta_{\sigma\pi}$ between the POAV1 and all three vectors of the surrounding atoms was calculated and checked to be equal according to:[5c]

$$\theta_{\sigma_i\pi} = cos^{-1}\left(\frac{\begin{bmatrix}x_i\\y_i\\z_i\end{bmatrix}\cdot\begin{bmatrix}x_\pi\\y_\pi\\z_\pi\end{bmatrix}}{\|\vec{V}_i\|\cdot\|\vec{V}_\pi\|}\right) \quad (9)$$

Example:

angle check	cos $\theta_{\sigma\pi}$	rad	degrees	Neg. Scalar
V1-p-Orbital	0.0948894	1.475764	84.555	95.445
V2-p-Orbital	0.0948894	1.475764	84.555	
V3-p-Orbital	0.0948894	1.475764	84.555	

When the angle turned out to be < 90° (as in the example) the scalar product was multiplied with -1.

The pyramidalisation θ was determined as $(\theta_{\sigma\pi} - 90)°$

The degree of hydridization (POAV1) of the π-orbital (s^mp) was calculated with:[5c]

$$m = 2\,cos^2(\theta_{\sigma\pi})/(1 - 3cos^2(\theta_{\sigma\pi})) \quad (10)$$

The average degree of hydridization of the σ-orbital (sp^n) was calculated with:[5c]

$$\bar{n} = 3m + 2 \quad (11)$$

The x, y and z coordinates for the POAV1-dummy atom were obtained after shifting the vector or its negative (in the case of an initial $\theta_{\sigma\pi} < 90°$, as in the example) back to the central atom by adding the x_c, y_c, and z_c values of the center.

Example:

POAV1-dummy	x	y	z
vector	-0.22198	0.049237	0.973806
shifted	-0.3656	0.7158	1.2850

For the parameters of the POAV2 theory first the cosine of the angle θ_{ij} between all combinations of the normalized vectors V_1, V2 and V3 were calculated according to:

$$\cos\theta_{ij} = \begin{bmatrix}x_i\\y_i\\z_i\end{bmatrix}\cdot\begin{bmatrix}x_j\\y_j\\z_j\end{bmatrix} \quad (12)$$

Example:

angle	V1-V2	V2-V3	V3-V1
cos	-0.560537	-0.308616	-0.576656
rad	2.165831	1.884534	2.1854265
degree	124.09297	107.9759	125.21571

The relation of the POAV2 to the vectors of the neighbouring atoms can be expressed in a set of linear homogenious equations:[5a]

$$(x_3 cos\theta_{12} - x_2 cos\theta_{31})x_\pi + (y_3 cos\theta_{12} - y_2 cos\theta_{31})y_\pi + (z_3 cos\theta_{12} - z_2 cos\theta_{31})z_\pi = 0$$
$$(x_1 cos\theta_{23} - x_3 cos\theta_{12})x_\pi + (y_1 cos\theta_{23} - y_3 cos\theta_{12})y_\pi + (z_1 cos\theta_{23} - z_3 cos\theta_{12})z_\pi = 0$$
$$(x_2 cos\theta_{13} - x_1 cos\theta_{23})x_\pi + (y_2 cos\theta_{13} - y_1 cos\theta_{23})y_\pi + (z_2 cos\theta_{13} - z_1 cos\theta_{23})z_\pi = 0 \qquad (13)$$

The constants in each equation were summarised in the form:

$$a_i x_\pi + b_i y_\pi + c_i z_\pi = 0 \qquad (14)$$

Example:

	a	b	c
Eq. 1	-0.87938	-0.189477	-0.19245
Eq. 2	0.3144588	0.71411	0.0110284
Eq. 3	0.5649213	-0.524633	0.1814211

One equation was solved for x_π in dependence of y_π and z_π and the result was substituted in another equation which was then solved for y_π in dependence of z_π, yielding the following relations:

$$x_\pi = -\frac{(b_i y_\pi + c_i z_\pi)}{a_i} \qquad (15) \qquad \text{and} \qquad y_\pi = \frac{(a_i c_j - a_j c_i)}{(a_j b_i - a_i b_j)} z_\pi \qquad (16)$$

By setting z_π to a constant value y_π and x_π may be obtained. In order to assure that the POAV2 points in the same direction as the POAV1 the z-coordinate of the POAV1 vector was used as the constant value for z_π.

The result was checked for consistency by solving for all combinations of the initial equations and the resultant vector was normalized.

Example:

Eq. 1&2		Z=Z(POAV1)	normed
x = -(b1y+c1z)/a1	X=	0.23187441	0.23076
y = z(a1c2-a2c1)/(a2b1-a1b2)	Y=	-0.087067	-0.08665
	Z=	-0.9738064	-0.96914
	magnitude	1.00481104	1

Eq. 1&3		Z=Z(POAV1)	normed
x = -(b1y+c1z)/a1	X=	0.23187441	0.23076
y = z(a1c3-a3c1)/(a3b1-a1b3)	Y=	-0.087067	-0.08665
	Z=	-0.9738064	-0.96914
	magnitude	1.00481104	1

Eq. 2&3		Z=Z(POAV1)	normed
x = -(b2y+c2z)/a2	X=	0.23187441	0.23076
y = z(a2c3-a3c2)/(a3b2-a2b3)	Y=	-0.087067	-0.08665
	Z=	-0.9738064	-0.96914
	magnitude	1.00481104	1

The x, y and z coordinates for the POAV2-dummy atom were obtained after shifting the vector or its negative (in the case of an initial $\theta_{\sigma\pi} < 90°$, as in the example) back to the central atom by adding the x_c, y_c, and z_c values of the center.

Example:

POAV2-dummy	x	y	z
vector	-0.23076	0.08665	0.96914
shifted	-0.37439	0.75325	1.28030

The POAV2 theory yields the individual σ-bond hybridizations (sp^n) through the following relations:[5a]

$$n_1 = \lambda_1^2 = \frac{-(cos\theta_{23})}{cos\theta_{12}cos\theta_{13}}, \qquad n_2 = \lambda_2^2 = \frac{-(cos\theta_{13})}{cos\theta_{12}cos\theta_{23}}, \qquad n_3 = \lambda_3^2 = \frac{-(cos\theta_{12})}{cos\theta_{13}cos\theta_{23}} \tag{17}$$

With $S(\lambda_\sigma) = \sum_{i=1}^{3} \frac{1}{1+\lambda_i^2}$ and the normalization requirement of the s content in the four hybrids $S(\lambda_\sigma) + \frac{1}{1+\lambda_\pi^2} = 1$ the p-orbital hybridization s^mp may be obtained according to:

$$m = \frac{1}{\lambda_\pi^2} = S(\lambda_\sigma)^{-1} - 1 \tag{18}$$

Example:

	1	2	3	Sum	
n	0.9547667	3.333446	3.149695		
lambda	0.9771216	1.825773	1.774738		
1/(1+n)	0.51157	0.230763	0.2409816	0.9833148	
(lambda pi)^2					58.933268
m					0.0169683

Complete list of determined angles and distances:

The POAV1 and POAV2 analysis was applied to the C2, C3, C8 and the N atom and their symmetric counterparts for the computed C_i and C_2 symmetric unsubstituted *N,N'*-diacetylindigo and the 5,5'- and 6,6'-bis-substituted *N,N'*-diacetylindigo compounds with 4-ethylpheny (PhEt) and 4-methoxyphenyl (PhOMe) substituents as well as the X-ray crystallographic determined molecular structures of *N,N'*-diacetylindigo (published by *Grimme*)[6] and the 5,5'- and 6,6'-bis-substituted *N,N'*-diacetylindigo compounds **12** and **23**. The definitions of the center atom and their surrounding neighbor atoms 1, 2 and 3 are given in **Table 9**. The primary data of the POAV1 and POAV2 analysis is complied in**Table 10** and Table 11. Finally, Table 12 summerises all measured distances and angles which were obtained after introduction of the POAV1 and POAV2 dummy atoms in the computed or X-ray crystallographic determined molecular structures.

Table 9: Definition of the center atoms and the three surrounding atoms on which the POAV analysis was applied.

Center	C2	C2'	N	N'	C3	C3'	C8	C8'
Atom 1	C2'	C2	C2	C2'	C2	C2'	C9	C9'
Atom 2	C3	C3'	C7a	C7a'	O(3)	O(3)'	N	N'
Atom 3	N	N'	C8	C8'	C3a	C3a'	O(8)	O(8)'

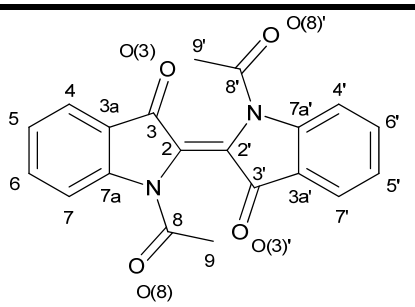


Table 10: Primary data of the POAV1 and POAV2 analysis for the computed C_i and C_2 symmetric unsubstituted *N,N'*-diacetylindigo and the 5,5'- and 6,6'-bis-substituted *N,N'*-diacetylindigo compounds with 4-ethylpheny (PhEt) and 4-methoxyphenyl (PhOMe) substituents.

Structure	Center	POAV1											POAV2											
		neighboring atoms angles, degree							dummy atom position				angles, degree								dummy atom position			
		θ_{12}	θ_{23}	θ_{31}	$\theta_{\sigma\pi}$	Pyr.	$\bar{n}$	m	x	y	z	r	POAV1	$\theta_{\sigma 1\pi}$	$\theta_{\sigma 2\pi}$	$\theta_{\sigma 3\pi}$	n_1	n_2	n_3	m	x	y	z	r
N,N'-	C2	126.23	107.05	126.44	91.71	1.71	2.005	0.00178	-0.17295	-1.14773	-0.39659	1	0.79	92.50	91.23	91.24	0.835	3.427	3.393	0.00159	-0.17940	-1.15079	-0.40843	1
DiAc	C2'	126.23	107.05	126.44	91.71	1.71	2.005	0.00178	0.17295	1.14773	0.39659	1	0.79	92.50	91.23	91.24	0.835	3.427	3.393	0.00159	0.17940	1.15079	0.40843	1
Indigo	⟨C2⟩	126.23	107.05	126.44	91.71	1.71	2.005	0.00178					0.79	92.50	91.23	91.24	0.835	3.427	3.393	0.00159				
C_i-sym.	N	108.26	118.41	128.75	97.07	7.07	2.095	0.03173	-1.99015	0.56372	-0.51992	1	2.79	96.30	94.79	99.60	2.426	4.197	1.052	0.02925	-1.97344	0.57791	-0.56337	1
	N'	108.26	118.41	128.75	97.07	7.07	2.095	0.03173	1.99015	-0.56372	0.51992	1	2.79	96.30	94.79	99.60	2.426	4.197	1.052	0.02925	1.97344	-0.57791	0.56337	1
	⟨N⟩	108.26	118.41	128.75	97.07	7.07	2.095	0.03173					2.79	96.30	94.79	99.60	2.426	4.197	1.052	0.02925				
	C3	126.51	128.71	104.78	90.23	0.23	2.000	0.00003	0.28088	-1.28543	-1.88521	1	0.13	90.15	90.36	90.15	4.120	0.686	3.729	0.00003	0.27871	-1.28532	-1.88463	1
	C3'	126.51	128.71	104.78	90.23	0.23	2.000	0.00003	-0.28088	1.28543	1.88521	1	0.13	90.15	90.36	90.15	4.120	0.686	3.729	0.00003	-0.27871	1.28532	1.88463	1
	⟨C3⟩	126.51	128.71	104.78	90.23	0.23	2.000	0.00003					0.13	90.15	90.36	90.15	4.120	0.686	3.729	0.00003				
	C8	118.01	119.22	122.07	92.77	2.77	2.014	0.00470	-2.54708	-0.35130	0.83812	1	0.20	92.80	92.58	92.91	1.957	2.316	1.812	0.00468	-2.54412	-0.35017	0.83666	1
	C8'	118.01	119.22	122.07	92.77	2.77	2.014	0.00470	2.54708	0.35130	-0.83812	1	0.20	92.80	92.58	92.91	1.957	2.316	1.812	0.00468	2.54412	0.35017	-0.83666	1
	⟨C8⟩	118.01	119.22	122.07	92.77	2.77	2.014	0.00470					0.20	92.80	92.58	92.91	1.957	2.316	1.812	0.00468				
N,N'-	C2	124.09	107.98	125.22	95.44	5.44	2.056	0.01851	-0.36561	0.71584	1.28497	1	2.22	97.66	94.09	94.21	0.955	3.333	3.150	0.01697	-0.37439	0.75325	1.28030	1
DiAc	C2'	124.09	107.98	125.22	95.44	5.44	2.056	0.01851	0.36561	-0.71584	1.28497	1	2.22	97.66	94.09	94.21	0.955	3.333	3.150	0.01697	0.37439	-0.75325	1.28030	1
Indigo	⟨C2⟩	124.09	107.98	125.22	95.44	5.44	2.056	0.01851					2.22	97.66	94.09	94.21	0.955	3.333	3.150	0.01697				
C_2-sym.	N	108.43	121.67	128.49	93.91	3.91	2.028	0.00941	1.26223	1.40021	-0.49993	1	1.57	93.26	92.75	95.43	2.668	3.749	0.968	0.00865	1.23947	1.40632	-0.51398	1
	N'	108.43	121.67	128.49	93.91	3.91	2.028	0.00941	-1.26223	-1.40021	-0.49993	1	1.57	93.26	92.75	95.43	2.668	3.749	0.968	0.00865	-1.23947	-1.40632	-0.51398	1
	⟨N⟩	108.43	121.67	128.49	93.91	3.91	2.028	0.00941					1.57	93.26	92.75	95.43	2.668	3.749	0.968	0.00865				
	C3	126.92	128.70	104.21	91.35	1.35	2.003	0.00111	-1.67700	1.55869	0.76054	1	0.80	90.84	92.14	90.88	4.239	0.654	3.914	0.00091	-1.66448	1.56467	0.76149	1
	C3'	126.92	128.70	104.21	91.35	1.35	2.003	0.00111	1.67700	-1.55869	0.76054	1	0.80	90.84	92.14	90.88	4.239	0.654	3.914	0.00091	1.66448	-1.56467	0.76149	1
	⟨C3⟩	126.92	128.70	104.21	91.35	1.35	2.003	0.00111					0.80	90.84	92.14	90.88	4.239	0.654	3.914	0.00091				
	C8	118.80	119.67	121.22	91.85	1.85	2.006	0.00208	2.48586	1.15871	0.44552	1	0.08	91.86	91.77	91.91	1.982	2.174	1.878	0.00208	2.48465	1.15823	0.44509	1
	C8'	118.80	119.67	121.22	91.85	1.85	2.006	0.00208	-2.48586	-1.15871	0.44552	1	0.08	91.86	91.77	91.91	1.982	2.174	1.878	0.00208	-2.48465	-1.15823	0.44509	1
	⟨C8⟩	118.80	119.67	121.22	91.85	1.85	2.006	0.00208					0.08	91.86	91.77	91.91	1.982	2.174	1.878	0.00208				
5,5'-	C2	124.06	107.98	125.17	95.52	5.52	2.057	0.01906	0.80244	2.44121	-0.07639	1	2.25	97.77	94.15	94.27	0.957	3.333	3.150	0.01748	0.84091	2.43642	-0.07053	1
DiPhEt-	C2'	124.05	107.98	125.17	95.52	5.52	2.057	0.01907	-0.80236	2.44133	0.07764	1	2.25	97.77	94.15	94.27	0.957	3.333	3.149	0.01749	-0.84083	2.43655	0.07179	1
N,N'-	⟨C2⟩	124.05	107.98	125.17	95.52	5.52	2.057	0.01906					2.25	97.77	94.15	94.27	0.957	3.333	3.150	0.01748				
DiAc	N	108.38	121.67	128.60	93.84	3.84	2.027	0.00908	0.82764	0.65976	1.69303	1	1.55	93.20	92.70	95.34	2.669	3.769	0.963	0.00834	0.84162	0.64581	1.67442	1
Indigo	N'	108.38	121.67	128.59	93.84	3.84	2.027	0.00908	-0.82778	0.66094	-1.69277	1	1.56	93.20	92.70	95.34	2.669	3.769	0.963	0.00834	-0.84176	0.64697	-1.67416	1
	⟨N⟩	108.38	121.67	128.60	93.84	3.84	2.027	0.00908					1.56	93.20	92.70	95.34	2.669	3.769	0.963	0.00834				
	C3	126.90	128.74	104.20	91.32	1.32	2.003	0.00107	2.07205	1.90863	-0.97898	1	0.78	90.82	92.11	90.86	4.249	0.653	3.913	0.00088	2.07292	1.90961	-0.96537	1
	C3'	126.91	128.73	104.19	91.33	1.33	2.003	0.00109	-2.07213	1.90836	0.98015	1	0.79	90.83	92.12	90.87	4.248	0.653	3.915	0.00090	-2.07302	1.90936	0.96643	1
	⟨C3⟩	126.91	128.73	104.19	91.33	1.33	2.003	0.00108					0.79	90.83	92.11	90.86	4.249	0.653	3.914	0.00089				
	C8	118.84	119.64	121.22	91.83	1.83	2.006	0.00204	0.15730	1.59979	2.74314	1	0.08	91.84	91.76	91.89	1.978	2.173	1.882	0.00204	0.15733	1.59936	2.74187	1
	C8'	118.84	119.65	121.21	91.82	1.82	2.006	0.00203	-0.15741	1.60157	-2.74211	1	0.08	91.83	91.75	91.88	1.979	2.171	1.882	0.00202	-0.15744	1.60114	-2.74086	1
	⟨C8⟩	118.84	119.64	121.21	91.83	1.83	2.006	0.00204					0.08	91.84	91.75	91.88	1.979	2.172	1.882	0.00203				

Continuation **Table 10**

Structure	Center	POAV1											POAV2											
		neighboring atoms							dummy atom position												dummy atom position			
		angles, degree											angles, degree											
		θ_{12}	θ_{23}	θ_{31}	$\theta_{\sigma\pi}$	Pyr.	$\bar{n}$	m	x	y	z	r	POAV1	$\theta_{\sigma 1\pi}$	$\theta_{\sigma 2\pi}$	$\theta_{\sigma 3\pi}$	n_1	n_2	n_3	m	x	y	z	r
5,5'-	C2	124.11	107.97	125.21	95.44	5.44	2.055	0.01847	0.80088	-2.48239	0.07835	1	2.22	97.65	94.09	94.20	0.954	3.332	3.153	0.01693	0.83887	-2.47774	0.07261	1
DiPhOMe-	C2'	124.11	107.97	125.21	95.44	5.44	2.056	0.01850	-0.80079	-2.48255	-0.07780	1	2.22	97.66	94.09	94.21	0.954	3.332	3.152	0.01696	-0.83880	-2.47789	-0.07207	1
N,N'-	⟨C2⟩	124.11	107.97	125.21	95.44	5.44	2.055	0.01848					2.22	97.66	94.09	94.20	0.954	3.332	3.153	0.01694				
DiAc	N	108.38	121.61	128.61	93.89	3.89	2.028	0.00934	0.83686	-0.70117	-1.69150	1	1.58	93.25	92.73	95.41	2.663	3.775	0.964	0.00857	0.85111	-0.68710	-1.67265	1
Indigo	N'	108.38	121.62	128.60	93.89	3.89	2.028	0.00934	-0.83690	-0.70073	1.69149	1	1.57	93.25	92.73	95.41	2.664	3.774	0.964	0.00857	-0.85115	-0.68668	1.67265	1
	⟨N⟩	108.38	121.61	128.61	93.89	3.89	2.028	0.00934					1.58	93.25	92.73	95.41	2.664	3.775	0.964	0.00857				
	C3	126.89	128.72	104.23	91.30	1.30	2.003	0.00103	2.06543	-1.95546	0.98645	1	0.77	90.81	92.07	90.85	4.239	0.655	3.902	0.00085	2.06633	-1.95646	0.97312	1
	C3'	126.89	128.72	104.23	91.30	1.30	2.003	0.00103	-2.06543	-1.95578	-0.98618	1	0.77	90.81	92.07	90.85	4.239	0.655	3.903	0.00085	-2.06633	-1.95678	-0.97284	1
	⟨C3⟩	126.89	128.72	104.23	91.30	1.30	2.003	0.00103					0.77	90.81	92.07	90.85	4.239	0.655	3.903	0.00085				
	C8	118.86	119.65	121.19	91.84	1.84	2.006	0.00207	0.16181	-1.64122	-2.74129	1	0.08	91.85	91.77	91.90	1.979	2.169	1.884	0.00206	0.16183	-1.64079	-2.74004	1
	C8'	118.86	119.64	121.19	91.84	1.84	2.006	0.00208	-0.16161	-1.64044	2.74156	1	0.08	91.86	91.77	91.90	1.979	2.169	1.885	0.00208	-0.16164	-1.64001	2.74031	1
	⟨C8⟩	118.86	119.64	121.19	91.84	1.84	2.006	0.00207					0.08	91.85	91.77	91.90	1.979	2.169	1.884	0.00207				
6,6'-	C2	124.19	108.03	125.08	95.43	5.43	2.055	0.01839	0.65198	0.46930	2.00998	1	2.20	97.63	94.10	94.19	0.958	3.305	3.159	0.01688	0.68750	0.48312	2.00545	1
DiPhEt-	C2'	124.19	108.03	125.08	95.43	5.43	2.055	0.01838	-0.65259	-0.46913	2.00979	1	2.20	97.63	94.10	94.19	0.958	3.305	3.159	0.01687	-0.68811	-0.48296	2.00525	1
N,N'-	⟨C2⟩	124.19	108.03	125.08	95.43	5.43	2.055	0.01839					2.20	97.63	94.10	94.19	0.958	3.305	3.159	0.01687				
DiAc	N	108.31	121.69	128.36	94.22	4.22	2.033	0.01101	1.57093	-1.05472	0.23555	1	1.71	93.51	92.97	95.88	2.695	3.761	0.963	0.01010	1.57363	-1.02936	0.21997	1
Indigo	N'	108.30	121.70	128.36	94.22	4.22	2.033	0.01100	-1.57098	1.05474	0.23497	1	1.71	93.51	92.97	95.88	2.696	3.761	0.963	0.01010	-1.57367	1.02937	0.21940	1
	⟨N⟩	108.30	121.69	128.36	94.22	4.22	2.033	0.01101					1.71	93.51	92.97	95.88	2.696	3.761	0.963	0.01010				
	C3	126.89	128.84	104.09	91.38	1.38	2.003	0.00116	1.29704	1.88945	1.48376	1	0.82	90.85	92.20	90.89	4.290	0.647	3.931	0.00095	1.30500	1.87755	1.48474	1
	C3'	126.89	128.84	104.10	91.38	1.38	2.003	0.00116	-1.29745	-1.88935	1.48350	1	0.82	90.86	92.20	90.89	4.289	0.647	3.930	0.00096	-1.30543	-1.87743	1.48448	1
	⟨C3⟩	126.89	128.84	104.10	91.38	1.38	2.003	0.00116					0.82	90.85	92.20	90.89	4.290	0.647	3.930	0.00095				
	C8	118.88	119.75	121.10	91.73	1.73	2.005	0.00182	1.52993	-2.28758	1.19531	1	0.07	91.73	91.67	91.78	1.989	2.155	1.885	0.00182	1.52933	-2.28663	1.19496	1
	C8'	118.88	119.75	121.10	91.73	1.73	2.006	0.00184	-1.53036	2.28780	1.19458	1	0.07	91.74	91.67	91.79	1.989	2.156	1.884	0.00183	-1.52976	2.28684	1.19423	1
	⟨C8⟩	118.88	119.75	121.10	91.73	1.73	2.005	0.00183					0.07	91.74	91.67	91.79	1.989	2.155	1.884	0.00183				
6,6'-	C2	124.36	108.00	125.00	95.37	5.37	2.054	0.01801	0.64575	2.14594	-0.24530	1	2.19	97.56	94.06	94.13	0.955	3.289	3.184	0.01652	0.68107	2.14325	-0.25949	1
DiPhOMe-	C2'	124.19	108.01	125.20	95.33	5.33	2.053	0.01771	-0.65036	2.03530	0.68916	1	2.17	97.50	94.01	94.12	0.955	3.318	3.153	0.01624	-0.68514	2.02917	0.70272	1
N,N'-	⟨C2⟩	124.27	108.00	125.10	95.35	5.35	2.054	0.01786					2.18	97.53	94.04	94.12	0.955	3.303	3.169	0.01638				
DiAc	N	108.30	121.67	128.36	94.25	4.25	2.033	0.01117	1.58398	0.21002	1.05357	1	1.72	93.54	92.99	95.92	2.695	3.764	0.964	0.01024	1.58654	0.19741	1.02636	1
Indigo	N'	108.29	121.65	128.37	94.28	4.28	2.034	0.01132	-1.58285	0.43010	-1.00511	1	1.74	93.56	93.01	95.96	2.693	3.769	0.964	0.01039	-1.58529	0.41163	-0.98118	1
	⟨N⟩	108.30	121.66	128.37	94.26	4.26	2.034	0.01124					1.73	93.55	93.00	95.94	2.694	3.767	0.964	0.01032				
	C3	126.84	128.86	104.12	91.38	1.38	2.004	0.00117	1.27846	1.79538	-1.72268	1	0.82	90.86	92.21	90.90	4.288	0.649	3.917	0.00096	1.28652	1.79501	-1.71079	1
	C3'	126.84	128.85	104.13	91.35	1.35	2.003	0.00112	-1.27297	1.36057	2.05226	1	0.81	90.84	92.16	90.88	4.286	0.649	3.916	0.00092	-1.28091	1.36276	2.04085	1
	⟨C3⟩	126.84	128.86	104.13	91.37	1.37	2.003	0.00114					0.81	90.85	92.18	90.89	4.287	0.649	3.916	0.00094				
	C8	118.88	119.79	121.04	91.80	1.80	2.006	0.00198	1.54356	1.02656	2.38956	1	0.07	91.80	91.74	91.85	1.995	2.149	1.885	0.00197	1.54293	1.02634	2.38858	1
	C8'	118.92	119.76	121.05	91.76	1.76	2.006	0.00190	-1.55411	1.52165	-2.12746	1	0.07	91.77	91.70	91.82	1.990	2.149	1.889	0.00190	-1.55351	1.52121	-2.12657	1
	⟨C8⟩	118.90	119.77	121.04	91.78	1.78	2.006	0.00194					0.07	91.79	91.72	91.84	1.993	2.149	1.887	0.00194				

Table 11: Primary data of the POAV1 and POAV2 analysis for the X-ray crystallographic determined molecular structures of *N,N'*-diacetylindigo (published by Grimme)[6] and the 5,5'- and 6,6'-bis-substituted *N,N'*-diacetylindigo compounds **12** and **23.**

Comp.	Center	POAV1											POAV2											
		neighboring atoms angles, degree							dummy atom position				angles, degree								dummy atom position			
		θ_{12}	θ_{23}	θ_{31}	$\theta_{\sigma\pi}$	Pyr.	$\bar{n}$	m	x	y	z	r	POAV1	$\theta_{\sigma1\pi}$	$\theta_{\sigma2\pi}$	$\theta_{\sigma3\pi}$	n_1	n_2	n_3	m	x	y	z	r
N,N'-	C2	124.52	108.07	123.60	96.46	6.46	2.079	0.02632	8.42217	3.11937	8.03551	1	2.55	99.01	95.04	94.92	0.989	3.149	3.302	0.02426	8.45932	3.13158	8.01416	1
DiAc	C2'	125.42	107.42	124.56	95.33	5.33	2.053	0.01774	7.03531	2.43044	8.39943	1	2.30	97.64	94.02	93.94	0.910	3.270	3.414	0.01608	6.99756	2.42371	8.41155	1
Indigo[6]	⟨C2⟩	124.97	107.74	124.08	95.90	5.90	2.066	0.02203					2.43	98.32	94.53	94.43	0.950	3.209	3.358	0.02017				
Grimme	N	107.59	122.11	126.80	96.19	6.19	2.072	0.02406	7.82106	2.57005	5.65320	1	2.60	94.96	94.40	98.74	2.936	3.730	0.949	0.02193	7.81903	2.61508	5.64837	1
	N'	108.21	121.48	127.24	95.79	5.79	2.063	0.02098	5.89487	4.66915	8.10428	1	2.30	94.80	94.14	98.03	2.760	3.708	0.989	0.01931	5.87312	4.64898	8.07714	1
	⟨N⟩	107.90	121.79	127.02	95.99	5.99	2.068	0.02252					2.45	94.88	94.27	98.39	2.848	3.719	0.969	0.02062				
	C3	126.71	129.37	103.42	92.28	2.28	2.010	0.00319	9.21620	4.58286	7.79759	1	1.43	91.36	93.71	91.44	4.571	0.612	4.060	0.00257	9.22059	4.56380	7.78206	1
	C3'	126.26	128.67	104.95	91.15	1.15	2.002	0.00080	5.86812	1.45561	7.81838	1	0.64	90.74	91.79	90.78	4.096	0.698	3.669	0.00068	5.86608	1.46369	7.82582	1
	⟨C3⟩	126.49	129.02	104.19	91.72	1.72	2.006	0.00200					1.04	91.05	92.75	91.11	4.333	0.655	3.864	0.00162				
	C8	118.54	118.94	122.40	91.14	1.14	2.002	0.00079	8.08390	1.06087	5.93190	1	0.08	91.17	91.05	91.18	1.890	2.318	1.843	0.00078	8.08346	1.06223	5.93194	1
	C8'	117.78	119.40	122.59	91.59	1.59	2.005	0.00154	6.83397	5.20427	9.29136	1	0.13	91.60	91.46	91.69	1.955	2.354	1.763	0.00153	6.83394	5.20290	9.28947	1
	⟨C8⟩	118.16	119.17	122.50	91.36	1.36	2.003	0.00116					0.11	91.39	91.26	91.44	1.923	2.336	1.803	0.00116				
12	C2	124.03	107.64	124.91	96.11	6.11	2.070	0.02349	12.91833	71.57718	10.94217	1	2.55	98.66	94.57	94.68	0.946	3.374	3.227	0.02145	12.93219	71.60857	10.91394	1
5,5'-subst.	C2'	124.64	107.98	123.83	96.24	6.24	2.074	0.02451	12.43868	70.21342	11.65598	1	2.50	98.74	94.83	94.73	0.976	3.173	3.308	0.02253	12.41539	70.18346	11.67757	1
	⟨C2⟩	124.33	107.81	124.37	96.18	6.18	2.072	0.02400					2.52	98.70	94.70	94.71	0.961	3.274	3.267	0.02199				
	N	108.53	122.60	128.41	92.23	2.23	2.009	0.00303	12.51651	70.52331	8.69723	1	0.90	91.83	91.59	93.11	2.729	3.629	0.949	0.00279	12.50734	70.53597	8.69573	1
	N'	108.04	122.76	128.24	93.21	3.21	2.019	0.00633	10.06826	70.99460	11.34552	1	1.35	92.59	92.26	94.53	2.823	3.693	0.925	0.00577	10.06691	70.97439	11.33358	1
	⟨N⟩	108.29	122.68	128.33	92.72	2.72	2.014	0.00468					1.12	92.21	91.93	93.82	2.776	3.661	0.937	0.00428				
	C3	126.07	128.98	104.72	91.59	1.59	2.005	0.00154	12.39060	73.09209	10.54827	1	0.90	91.00	92.49	91.07	4.206	0.686	3.685	0.00129	12.40094	73.08407	10.53954	1
	C3'	126.24	128.85	104.66	91.64	1.64	2.005	0.00165	12.16078	68.60370	11.40890	1	0.94	91.04	92.58	91.10	4.192	0.683	3.724	0.00138	12.15111	68.61248	11.41874	1
	⟨C3⟩	126.15	128.91	104.69	91.62	1.62	2.005	0.00159					0.92	91.02	92.53	91.09	4.199	0.684	3.704	0.00134				
	C8	117.53	119.00	122.88	92.57	2.57	2.012	0.00403	13.48982	69.32981	9.12114	1	0.24	92.61	92.33	92.74	1.932	2.423	1.756	0.00401	13.48690	69.33251	9.12262	1
	C8'	116.32	120.05	123.22	92.12	2.12	2.008	0.00275	10.46849	72.29762	12.18886	1	0.26	92.08	91.90	92.35	2.062	2.468	1.616	0.00273	10.47121	72.29520	12.18616	1
	⟨C8⟩	116.92	119.52	123.05	92.34	2.34	2.010	0.00339					0.25	92.35	92.12	92.55	1.997	2.446	1.686	0.00337				
23	C2	125.13	108.27	123.89	95.44	5.44	2.055	0.01846	49.57513	6.61039	-14.47354	1	2.15	97.58	94.26	94.12	0.977	3.090	3.292	0.01702	49.58717	6.58496	-14.49829	1
6,6'-subst.	C2'	125.85	108.12	123.06	95.70	5.70	2.061	0.02031	49.36012	7.96825	-13.68789	1	2.28	97.96	94.53	94.22	0.973	2.995	3.453	0.01868	49.35410	7.99299	-13.65731	1
	⟨C2⟩	125.49	108.19	123.47	95.57	5.57	2.058	0.01939					2.21	97.77	94.39	94.17	0.975	3.043	3.373	0.01785				
	N	107.02	121.00	123.78	99.54	9.54	2.180	0.05992	51.77703	7.61165	-15.24509	1	3.88	97.57	97.01	103.40	3.164	3.687	1.022	0.05492	51.80371	7.56319	-15.20596	1
	N'	107.48	122.06	124.48	98.12	8.12	2.127	0.04240	50.40171	6.76757	-11.71324	1	3.28	96.41	96.01	101.38	3.121	3.550	1.000	0.03892	50.44318	6.80609	-11.72179	1
	⟨N⟩	107.25	121.53	124.13	98.83	8.83	2.153	0.05116					3.58	96.99	96.51	102.39	3.143	3.618	1.011	0.04692				
	C3	127.14	128.60	104.01	91.66	1.66	2.005	0.00168	49.95339	5.00937	-14.34430	1	0.99	91.03	92.65	91.06	4.269	0.643	3.998	0.00138	49.95912	5.01844	-14.35794	1
	C3'	127.22	128.39	104.18	91.50	1.50	2.004	0.00138	49.90074	9.50331	-13.42855	1	0.89	90.94	92.39	90.97	4.191	0.652	3.977	0.00113	49.89556	9.49503	-13.41649	1
	⟨C3⟩	127.18	128.49	104.09	91.58	1.58	2.005	0.00153					0.94	90.99	92.52	91.02	4.230	0.647	3.987	0.00125				
	C8	117.70	119.18	123.02	91.05	1.05	2.002	0.00067	50.86915	8.55931	-16.19589	1	0.10	91.06	90.95	91.12	1.924	2.404	1.750	0.00066	50.86958	8.55856	-16.19441	1
	C8'	117.53	119.76	122.48	91.61	1.61	2.005	0.00159	49.06390	5.87049	-11.73359	1	0.14	91.61	91.49	91.73	2.000	2.340	1.734	0.00158	49.06552	5.87146	-11.73513	1
	⟨C8⟩	117.62	119.47	122.75	91.33	1.33	2.003	0.00113					0.12	91.34	91.22	91.42	1.962	2.372	1.742	0.00112				

Table 12: Intramolecular distances and angles in the computed C_i and C_2 symmetric unsubstituted *N,N'*-diacetyl indigo and the X-ray crystallographic determined molecular structures of *N,N'*-diacetyl indigo (published by Grimme)[6] and the 5,5'- and 6,6'-bis-substituted *N,N'*-diacetyl indigo compounds **12** and **23** after introduction of the POAV1 and POAV2 dummy atoms.

Dist./Angle/Dihedral	Function	C_i	C_2	Grimme[6]	**12** (5,5')	**23** (6,6')
C2	Pyramidalization θ_{C2} [°] POAV1			6.46	6.12	5.44
C2'				5.33	6.24	5.70
Av.		1.71	5.45	5.90	6.18	5.57
N	Pyramidalization θ_N [°] POAV1			6.19	2.23	9.54
N'				5.79	3.21	8.12
Av.		7.07	3.91	5.99	2.72	8.83
C3	Pyramidalization θ_{C3} [°] POAV1			2.29	1.59	1.66
C3'				1.15	1.64	1.50
Av.		0.23	1.35	1.72	1.62	1.58
C8	Pyramidalization θ_{C8} [°] POAV1			1.14	2.57	1.05
C8'				1.59	2.12	1.61
Av.		2.77	1.85	1.36	2.34	1.33
C2=C2'	Distance $d_{C2-C2'}$ [Å]	1.362	1.364	1.349	1.362	1.351
C2-C3	Distance d_{C2-C3} [Å]			1.499	1.504	1.503
C2'-C3'				1.502	1.493	1.497
Av.		1.514	1.509	1.501	1.499	1.500
N-C7a	Distance d_{N-C7a} [Å]			1.426	1.429	1.433
N'-C7a'				1.426	1.428	1.433
Av.		1.427	1.429	1.426	1.428	1.433
N-C2	Distance d_{N-C2} [Å]			1.414	1.413	1.419
N'-C2'				1.413	1.413	1.417
Av.		1.413	1.407	1.414	1.413	1.418
N-C8	Distance d_{N-C8} [Å]			1.411	1.418	1.418
N'-C8'				1.412	1.420	1.406
Av.		1.438	1.424	1.411	1.419	1.412
C2(p)-C2-C2'-C2(p)'	Twist $\Theta_{C2-C2'}$ [°] POAV1	180.00	-23.96	-19.54	-19.46	-20.06
C2(p)-C2-C2'-C2(p)'	Twist $\Theta_{C2-C2'}$ [°] POAV2	180.00	-24.15	-19.37	-19.46	-19.71
C3(p)-C3-C2-C2(p)	p-orbital overlap Θ_{C2-C3} [°] POAV1	12.18	13.59	18.39	12.25	16.11
C3(p)'-C3'-C2'-C2(p)'		-12.18	13.59	11.78	15.33	16.59
Av.		±12.18	13.59	15.09	13.79	16.35
C3(p)-C3-C2-C2(p)	p-orbital overlap Θ_{C2-C3} [°] POAV2	11.64	12.44	17.36	10.90	15.09
C3(p)'-C3'-C2'-C2(p)'		-11.64	12.44	10.37	13.97	15.32
Av.		±11.64	12.44	13.87	12.44	15.21
N(p)-N-C2-C2(p)	p-orbital overlap Θ_{C2-N} [°] POAV1	155.78	158.77	148.97	162.67	147.82
N(p)'-N'-C2'-C2(p)'		-155.78	158.77	158.10	158.89	150.15
Av.		±155.78	158.77	153.54	160.78	148.99
N(p)-N-C2-C2(p)	p-orbital overlap Θ_{C2-N} [°] POAV2	159.12	162.06	153.31	165.59	152.91
N(p)'-N'-C2'-C2(p)'		-159.12	162.06	162.03	162.01	154.72
Av.		±159.12	-162.06	157.67	163.80	153.82
N(p)-N-C8-C8(p)	p-orbital overlap Θ_{N-C8} [°] POAV1	-37.15	-20.58	-13.81	-31.66	-14.10
N(p)'-N'-C8'-C8(p)'		37.15	-20.58	-26.18	-30.70	-19.37
Av.		±37.15	-20.58	-20.00	-31.18	-16.74
N(p)-N-C8-C8(p)	p-orbital overlap Θ_{N-C8} [°] POAV2	-38.40	-21.02	-14.27	-31.92	-14.59
N(p)'-N'-C8'-C8(p)'		38.40	-21.02	-26.70	-31.11	-19.76
Av.		±38.40	-21.02	-20.49	-31.52	-17.18
Ln (5/6-5'/6') to Ln(2-2')	Skew σ [°]	11.63	4.28	7.37	3.91	5.86
Tor: 5-6-5'-6'	Effective ring twist α [°]	0.00	-24.67	-19.17	-26.05	-18.68
Ln (5-7a) to Ln (5'-7a')	Specific bent β_{C5} [°]	0.00	49.14	52.90	50.60	54.29
Ln (3a-6) to Ln (3a'-6')	Specific bent β_{C6} [°]	0.00	23.45	32.44	26.11	32.41
Ln(5/6-3a/7a) to Ln(2-2')		15.12	21.83	34.53	22.13	26.34
Ln(5'/6'-3a'/7a') to Ln(2-2')		-15.12	21.83	16.91	23.58	26.56
Sum	Overall bent γ	0	43.65	51.44	45.71	52.90

"p" denotes the POAV dummy atom of the appendent atom. "Ln" denotes a line which was defined to pass through the specified atoms. X/Y indicates that the centre between X and Y. The angle between the lines was determined using the Diamond 3 software from *Crystal Impact*.

Table 13: Intramolecular distances and angles in the computed C_2 symmetric molecular structures of 5,5'- and 6,6'-bis-substituted *N,N'*-diacetyl indigo compounds with 4-ethylpheny (PhEt) and 4-methoxyphenyl (PhOMe) substituents after introduction of the POAV1 and POAV2 dummy atoms.

Dist./Angle/Dihedral	Function	5,5'-DiPhEt	5,5'-DiPhOMe	6,6'-DiPhEt	6,6'-DiPhOMe
C2	Pyramidalization θ_{C2} [°] POAV1	5.52	5.44	5.43	5.37
C2'		5.52	5.44	5.43	5.33
Av.		5.52	5.44	5.43	5.35
N	Pyramidalization θ_{N} [°] POAV1	3.84	3.89	4.22	4.25
N'		3.84	3.89	4.22	4.28
Av.		3.84	3.89	4.22	4.26
C3	Pyramidalization θ_{C3} [°] POAV1	1.32	1.30	1.38	1.38
C3'		1.33	1.30	1.38	1.35
Av.		1.33	1.30	1.38	1.37
C8	Pyramidalization θ_{C8} [°] POAV1	1.83	1.84	1.73	1.80
C8'		1.82	1.84	1.73	1.76
Av.		1.83	1.84	1.73	1.78
C2=C2'	Distance $d_{C2\text{-}C2'}$ [Å]	1.364	1.364	1.363	1.363
C2-C3	Distance $d_{C2\text{-}C3}$ [Å]				
C2'-C3'					
Av.		1.510	1.510	1.510	1.510
N-C7a	Distance $d_{N\text{-}C7a}$ [Å]				
N'-C7a'					
Av.		1.428	1.428	1.429	1.429
N-C2	Distance $d_{N\text{-}C2}$ [Å]				
N'-C2'					
Av.		1.407	1.407	1.409	1.409
N-C8	Distance $d_{N\text{-}C8}$ [Å]				
N'-C8'					
Av.		1.423	1.422	1.422	1.422
C2(p)-C2-C2'-C2(p)'	Twist $\Theta_{C2\text{-}C2'}$ [°] POAV1	-24.40	-24.34	-24.15	-23.55
C2(p)-C2-C2'-C2(p)'	Twist $\Theta_{C2\text{-}C2'}$ [°] POAV2	-24.60	-24.53	-24.30	-23.69
C3(p)-C3-C2-C2(p)	p-orbital overlap $\Theta_{C2\text{-}C3}$ [°] POAV1				13.61
C3(p)'-C3'-C2'-C2(p)'					13.55
Av.		13.62	13.28	13.79	13.58
C3(p)-C3-C2-C2(p)	p-orbital overlap $\Theta_{C2\text{-}C3}$ [°] POAV2				12.44
C3(p)'-C3'-C2'-C2(p)'					12.49
Av.		12.44	12.11	12.66	12.47
N(p)-N-C2-C2(p)	p-orbital overlap $\Theta_{C2\text{-}N}$ [°] POAV1				158.29
N(p)'-N'-C2'-C2(p)'					158.09
Av.		158.80	159.04	158.17	158.19
N(p)-N-C2-C2(p)	p-orbital overlap $\Theta_{C2\text{-}N}$ [°] POAV2				161.67
N(p)'-N'-C2'-C2(p)'					161.47
Av.		162.10	162.33	161.55	161.57
N(p)-N-C8-C8(p)	p-orbital overlap $\Theta_{N\text{-}C8}$ [°] POAV1				-20.03
N(p)'-N'-C8'-C8(p)'					-20.15
Av.		-20.04	-20.31	-19.60	-20.09
N(p)-N-C8-C8(p)	p-orbital overlap $\Theta_{N\text{-}C8}$ [°] POAV2				-20.50
N(p)'-N'-C8'-C8(p)'					-20.61
Av.		-20.48	-20.75	-20.06	-20.55
Ln (5/6-5'/6') to Ln(2-2')	Skew σ [°]	4.20	4.06	4.69	4.59
Tor: 5-6-5'-6'	Effective ring twist α [°]	-26.08	-25.80	-23.95	-22.59
Ln (5-7a) to Ln (5'-7a')	Specific bent β_{C5} [°]	49.97	48.54	50.07	49.01
Ln (3a-6) to Ln (3a'-6')	Specific bent β_{C6} [°]	23.83	22.74	24.04	24.13
Ln(5/6-3a/7a) to Ln(2-2')		22.15	21.38	22.39	21.91
Ln(5'/6'-3a'/7a') to Ln(2-2')		22.14	21.37	22.40	22.28
Sum	Overall bent γ	44.29	42.75	44.79	44.20

"p" denotes the POAV dummy atom of the appendent atom. "Ln" denotes a line which was defined to pass through the specified atoms. X/Y indicates that the centre between X and Y. The angle between the lines was determined using the Diamond 3 software from *Crystal Impact*.

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