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Synthesis of a new class of electron rich chiral cyclophanes with large cavities

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Abstract—BINOL based electron rich chiral cyclophanes possessing large cavities have been synthesized starting from *m*-terphenyl dibromide and methyl *m*-/*p*-cinnamate. The presence of double bonds in the chiral cyclophanes makes them electron rich as revealed by C–T complexation studies of such cyclophanes donors with guests like TCNE, TCNQ and DDQ. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The design of organic molecules possessing functional groups that can interact with guest molecules in complementary ways is a challenge in organic chemistry.[1] The synthesis of BINOL based crown ethers was pioneered by Cram[2] and the chiral discriminating properties of BINOL are being exploited in modern organic synthesis and in asymmetric catalysis.[3] Electron rich cyclophanes bearing acetylenic units were reported by Whitlock.[4] Although chiral cyclophanes based on BINOL were earlier reported from our laboratory,[5] the synthesis of electron rich chiral cyclophanes with ethylene units would be more promising as they could form complexes with electron deficient guest molecules. Herein, we report the synthesis and CT complexation studies of electron rich BINOL based chiral cyclophanes.

2. Results and discussion

The *m*-terphenyl bromide **1** was synthesized employing the Hart reaction.[6] The treatment of *m*-terphenyl dibromide **1** with *p*-hydroxybenzaldehyde in DMF in the presence of K_2CO_3 at 60°C for 48 h gave dialdehyde **2** in good yield. The dialdehyde **2** was reduced to diol **3** using $NaBH_4$ in methanol and the diol **3** was converted into dibromide **4** using PBr_3 in CH_2Cl_2 at rt for 12 h. Dibromide **4** was then coupled with (*S*)-BINOL in acetone in the presence of K_2CO_3 under high dilution conditions to afford the chiral cyclophane **5** in 38% yield (Scheme 1).

The chiral cyclophane **5**, in its ^{1}H NMR, signals for the methylene protons merged to appear as multiplet in the region δ 4.90–5.90, not as in the case of chiral cyclophanes reported earlier,[5a] where the methylene protons appear as clear doublets. The aromatic protons appear in the region between δ 7.37–7.87. In ^{13}C NMR, the cyclophane **5** showed 22 signals for aromatic carbons in addition to benzylic carbons at δ 70.1 and 70.7. The momeric structure was supported by the FAB-MS spectrum, which showed the molecular ion peak at *m*/*z* 752. The compound had a specific rotation of -186 (*c* 0.4, $CHCl_3$). This cyclophane has a large cavity size and hence may bind bigger guest molecules when compared with chiral cyclophanes reported earlier.[5a]

In order to further increase the cavity size, methyl *m*-/*p*-hydroxycinnamate were used as spacer units. Treatment of the dibromide **1** with methyl *m*-hydroxycinnamate in DMF at 60°C for 48 h gave diester **6a** in good yield. Diol **7a** obtained by the reduction of diester **6a** using LAH in THF was converted to dibromide **8a** by treatment with PBr_3 in CH_2Cl_2 at rt for 12 h. Coupling dibromide **8a** with (*S*)-BINOL in acetone in the presence of K_2CO_3 gave chiral cyclophane **9a** in 21% yield. When a similar sequence was applied for methyl *p*-hydroxycinnamate, cyclophane **9b** was obtained in 16% yield (Scheme 2).

Cyclophanes **9a** and **9b** had optical rotations of -136.4 (*c* 0.4, $CHCl_3$) and -120.0 (*c* 0.4, $CHCl_3$) respectively. Cyclophanes **9a** and **9b** were characterized by ^{1}H, ^{13}C NMR and elemental analysis. The monomeric structures of cyclophanes **9a**, **b** were evidenced by FAB-MS.

2.1. Complexation studies

The presence of the double bond in cyclophanes **9a** and **9b** makes them electron rich hence may act as molecular receptors for electron deficient guest molecules. In order to

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Keywords: chiral cyclophanes; electron rich; large cavities.

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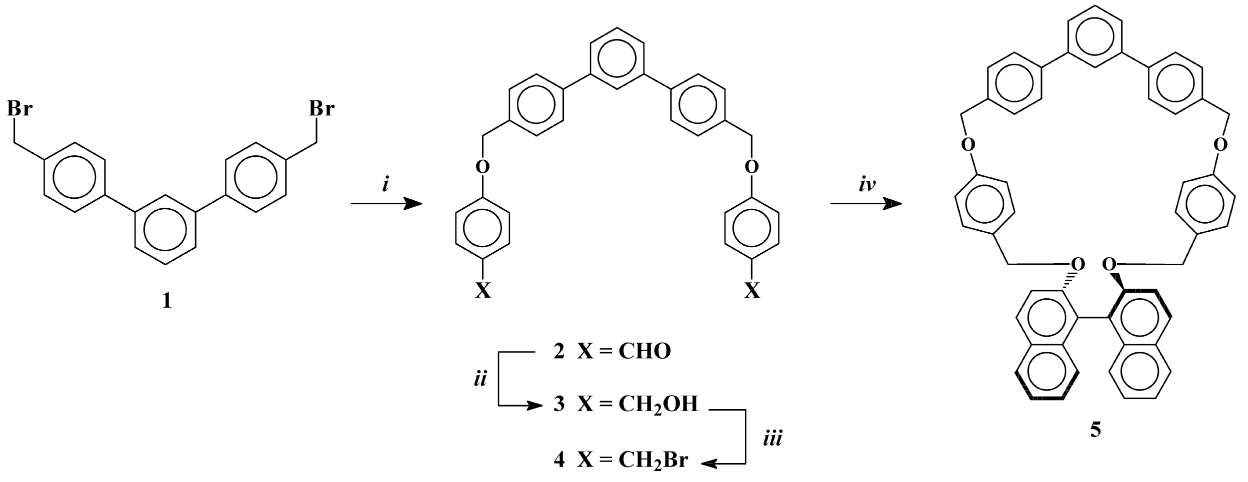
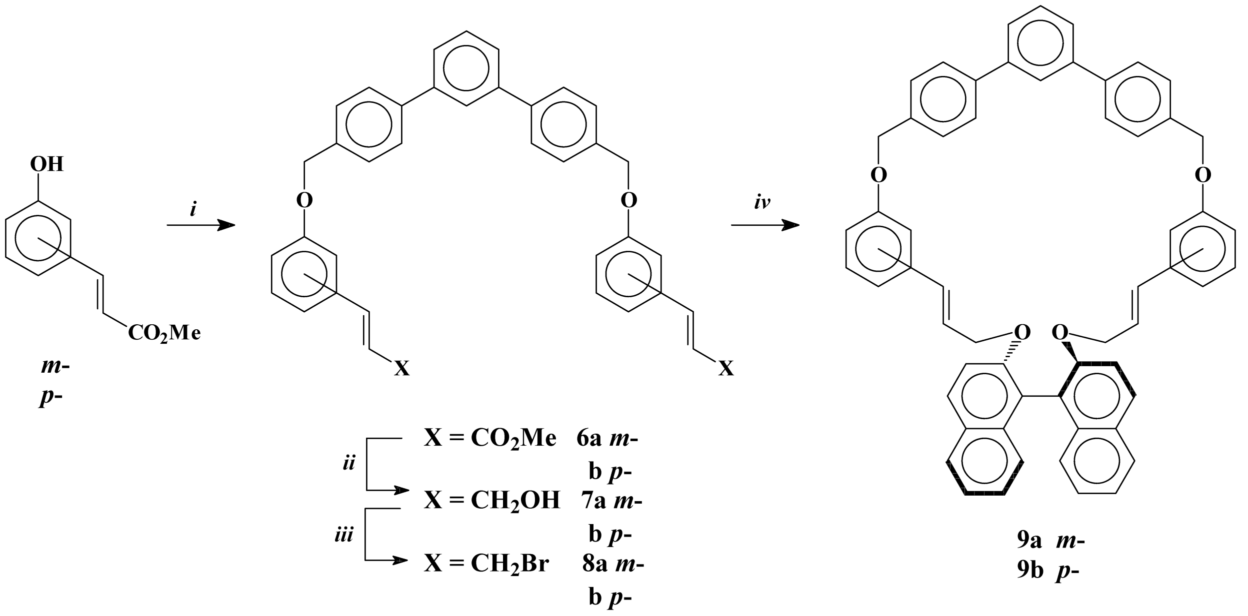


Scheme 1. *Reagents and conditions*: (i) 2.2 equiv. *p*-hydroxybenzaldehyde, K_2CO_3, DMF, 60°C, 48 h, 77%; (ii) $NaBH_4$, MeOH, 0°C, 6 h, 95%; (iii) PBr_3, CH_2Cl_2, 0°C, 92%; (iv) (*S*)-BINOL, K_2CO_3, acetone, rt, 120 h, 38%.



Scheme 2. *Reagents and conditions*: (i) 2.2 equiv. methyl *m*-/*p*-hydroxycinnamate, K_2CO_3, DMF, 60°C, 48 h, 56/46% (*m*-/*p*-); (ii) LAH, THF, rt, 6 h, 51/57% (*m*-/*p*-); (iii) PBr_3, CH_2Cl_2, 0°C, 46/38% (*m*-/*p*-); (iv) (*S*)-BINOL, K_2CO_3, acetone, rt, 120 h, 21/16% (*m*-/*p*-).

test the formation of charge transfer (CT) complexes, studies were carried out using the cyclophanes **9a** and **9b** with small molecules viz., TCNE, TCNQ, DDQ, DIPY in $CHCl_3/CH_3CN$ (4:1).

The UV–visible spectra of the CT complex of cyclophanes **9a** and **9b** with TCNE individually showed two absorbance maxima at 416 nm and 398 nm. The K_a values were determined using the Benesi-Hildebrand equation.[7] The association constant (K_a) was found to be 59 and 62 M^{-1} for CT complexes of cyclophane **9a** and **9b** with TCNE respectively. Complexation studies were also attempted with cyclophanes **9a** and **9b** and other guest molecules such as TCNQ, DDQ and DIPY. Appreciable changes were not observed in the UV–visible spectra of the cyclophanes **9a** and **9b** with TCNQ, DDQ and DIPY.

Further syntheses of electron rich chiral cyclophanes and their complexation studies with chiral guest molecules are under progress.

3. Experimental

3.1. General

All the melting points are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX 400 NMR spectrometer at 400 and 100.4 MHz respectively and coupling constants (*J*) are expressed in Hertz. The mass spectra were recorded on JEOL JMS-DX 303 HF (EI, 70 eV) and FAB-MS on JEOL SX 102/DA-6000 using *m*-nitrobenzyl alcohol (NBA) as matrix. The optical rotations were recorded on an Autopol-II automatic spectropolarimeter with cell length 10 cm using the D-line of sodium at 25°C. The organic extracts of crude products were dried over anhydrous sodium sulfate. Column chromatography was carried out with silica gel (ACME, 100–200 mesh). *m*-Terphenyl dibromide was synthesized following the literature procedure.[6a]

3.1.1. Dialdehyde 2. To a solution of *m*-terphenyl dibromide (4.16 g, 10 mmol) in DMF was added *p*-hydroxybenzaldehyde (2.564 g, 21 mmol) and anhydrous K_2CO_3 (14.0 g) and the reaction mixture was stirred at 60°C for 48 h. Then, the reaction mixture was added to a large amount of water (1 L) and digested over a water bath for 30 min. The residue obtained was extracted with $CHCl_3$ (4×100 mL) and the extracts were washed with water (3×100 mL); with brine (200 mL) and dried. Evaporation of the organic layer gave the dialdehyde **2**, which was purified over silica gel using hexane/$CHCl_3$ (1:1). Colourless solid; yield 77%; mp 205°C; IR (KBr, cm^{-1}) 3050, 1682 (C=O), 1605; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (s, 4H); 7.09 (d, 4H, *J*=8.8 Hz); 7.52 (d, 4H, *J*=8.3 Hz); 7.57 (d, 2H, *J*=4 Hz); 7.59 (t, 1H, *J*=4 Hz); 7.67 (d, 4H, *J*=8.3 Hz); 7.79 (s, 1H); 7.84 (d, 4H, *J*=8.8 Hz); 9.88 (s, 2H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 69.9, 115.1, 125.9, 126.3, 127.5, 128.0, 129.3, 130.1, 131.9, 135.1, 141.1, 141.2, 163.6, 190.7; *m/z* (EI, 70 eV) 498 (M$^+$, 5), 369 (17), 302 (5), 271 (100), 200 (9), 165 (17), 87 (27). Anal. Calcd for $C_{34}H_{26}O_{4:}$C, 81.91; H, 5.26. Found: C, 81.85; H, 5.27.

3.1.2. Diol 3. To a solution of the dialdehyde **2** (3.984 g, 8 mmol) in methanol (70 mL) was added in portions $NaBH_4$ (0.151 g, 4 mmol) at 0°C. The reaction mixture was stirred at rt for 6 h, after which conc. HCl (10 drops) was added. The residue obtained was filtered off. Evaporation of the solvent in *vacuo* gave the diol **3**, which was recrystallized from $CHCl_3$/MeOH (5:1). Yield 95%; mp 208°C (lit.[6b] 208°C).

3.1.3. Dibromide 4. To a stirred suspension of diol **4** (3.012 g, 6 mmol) in CH_2Cl_2 (120 mL), PBr_3 (0.3 mL, 3 mmol) was added and the reaction mixture was stirred at 0°C for 12 h. The reaction was poured into water (500 mL) and the organic layer was washed with water (3×150 mL); with brine (200 mL) and dried. The solvent was evaporated in *vacuo* to give dibromide **4**, which was recrystallized from hexane/CH_2Cl_2 (1:5). Colourless solid; yield 92%; mp 142°C; IR (KBr, cm^{-1}) 3050, 1605; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (s, 4H); 5.01 (s, 4H); 6.70–6.81 (m, 4H); 7.02–7.48 (m, 16H); *m/z* (FAB-MS) 632 (M$^+$+ 4); 630 (M$^+$+2); 628 (M$^+$). Anal. Calcd for $C_{34}H_{28}O_2Br_2$: C, 64.99; H, 4.49. Found: C, 65.12; H, 4.62.

3.1.4. Cyclophane 5. Dibromide **4** (0.314 g, 0.5 mmol) and (*S*)-BINOL (0.143 g, 0.5 mmol) were stirred with K_2CO_3 (20 mmol) in acetone (400 mL) at room temperature for 120 h, after which the reaction mixture was acidified and evaporated to dryness. The residue obtained was extracted with CH_2Cl_2 (3×100 mL), washed with 10% NaOH (2×50 mL); with water (3×100 mL) and dried ($MgSO_4$). Evaporation of the organic layer gave a residue, which was chromatographed over SiO_2 using hexane/$CHCl_3$ (1:1) to afford the chiral cyclophane **5** as a colourless solid. Yield 38%; mp 178°C; $[\alpha]_D^{25}$=-186 (*c* 0.4, $CHCl_3$); IR (KBr, cm^{-1}) 3050, 1605; ^{1}H NMR δ 4.90–5.90 (m, 8H); 6.86–7.38 (m, 20H); 7.77–7.87 (m, 12H); ^{13}C NMR δ 70.1, 70.7, 110.9, 115.5, 120.5, 123.7, 124.8, 124.9, 125.3, 125.5, 125.8, 126.7, 126.8, 127.1, 127.4, 128.1, 128.4, 129.3, 130.8, 133.4, 134.3, 136.6, 140.5, 153.7; *m/z* (FAB-MS) 752 (M$^+$). Anal. Calcd for $C_{54}H_{40}O_{4:}$ C, 86.14; H, 5.36. Found: C, 86.09; H, 5.38.

3.1.5. Diester 6a. *m*-Terphenyl dibromide (4.16 g, 10 mmol) and methyl *m*-hydroxycinnamate (3.76 g, 21 mmol) in dry DMF (40 mL) was treated with anhydrous K_2CO_3 (14 g) at 60°C for 48 h. Then, the reaction mixture was worked up as described for dialdehyde **4**. The crude product was purified over silica using hexane/$CHCl_3$ (1:2) to afford the diester **6a** as a colourless solid. Yield 56%; mp 192–194°C; IR (KBr, cm^{-1}) 3050, 1704 (C=O), 1600; ^{1}H NMR δ 3.79 (s, 6H); 5.12 (s, 4H); 6.42 (d, 2H, *J*=16.1 Hz); 7.02 (d, 2H, *J*=4 Hz); 7.13 (d, 4H, *J*=4 Hz); 7.23 (s, 1H); 7.30 (t, 2H, *J*=4 Hz); 7.52 (d, 4H, *J*=7.8 Hz); 7.58 (d, 2H, *J*=6.8 Hz); 7.63 (s, 1H); 7.66 (d, 4H, *J*=7.8 Hz); 7.80 (s, 2H); ^{13}C NMR δ 51.7, 69.7, 114.0, 116.9, 118.1, 121.0, 125.9, 126.2, 127.5, 127.9, 129.2, 129.9, 135.8, 140.9, 141.3, 144.7, 158.9, 167.3, 196.4; *m/z* (EI, 70 eV) 610 (M$^+$, 6), 562 (15), 537 (14), 471 (20), 467 (100), 386 (11), 366 (70), 271 (56), 257 (72), 236 (36), 184 (74), 149 (84), 158 (46). Anal. Calcd for $C_{40}H_{34}O_6$: C, 78.67; H, 5.61. Found: C, 78.62; H, 5.58.

3.1.6. Diester 6b. *m*-Terphenyl dibromide (4.16 g, 0.01 mol) and methyl *p*-hydroxycinnamate (3.76 g, 0.021 mol) was treated as described above. The crude product was chromatographed over silica using hexane/$CHCl_3$ (1:2) to afford the diester **6b** as a colourless solid. Yield 43%; mp 177°C; IR (KBr, cm^{-1}) 3050, 1690 (C=O), 1600; ^{1}H NMR δ 3.52 (s, 6H); 5.07 (s, 4H); 6.24 (d, 2H, *J*=15.6 Hz); 6.72–6.93 (m, 4H), 7.17–7.92 (m, 18H); ^{13}C NMR δ 59.6, 69.8, 115.2, 117.5, 126.3, 127.1, 127.5, 127.9, 128.3, 128.9, 129.3, 130.3, 135.6, 141.3, 144.4, 160.5, 193.3. *m/z* (EI, 70 eV) 610 (M$^+$, 8), 562 (12), 551 (7), 525 (24), 492 (41), 386 (17), 288 (62), 243 (24), 184 (76), 153 (36). Anal. Calcd for $C_{40}H_{34}O_6$/C, 78.67; H, 5.61. Found: C, 78.63; H, 5.59.

3.1.7. Diol 7a. To a solution of diester **6a** (8.418 g, 13.8 mmol) in dry THF (300 mL) was added in portions lithium aluminium hydride (0.656 g, 17.3 mmol) at 0°C. The reaction mixture was stirred at rt for 6 h and then run into $Na_2SO_4.10H_2O$ (20 g) and stirred. The mixture was then digested on a steam bath (20 min) and filtered. The inorganic residue was further extracted (Soxhlet) with THF (200 mL). The combined THF fractions, on evaporation, gave the corresponding alcohol, which was purified by recrystallization from a minimum volume of THF/MeOH (4:1). Colourless solid; yield 51%; mp 212°C; IR (KBr, cm^{-1}) 3300, 3050, 1626, 1600; ^{1}H NMR (DMSO-*d*$_6$) δ 5.08 (s, 4H); 5.37–5.41 (m, 4H); 6.72 (bs, 2H, exchangeable with D_2O); 6.92–8.01 (m, 24H); *m/z* (EI, 70 eV) 554 (M$^+$, 11), 499 (6), 478 (14), 445 (4), 413 (23), 384 (62), 308 (18), 288 (41), 229 (100), 184 (36), 153 (42). Anal. Calcd For $C_{38}H_{34}O_4$: C, 82.28; H, 6.18. Found: C, 82.14; H, 6.07.

3.1.8. Diol 7b. Following the procedure as above, the treatment of diester **6b** with lithium aluminium hydride gave the diol **7b** as a colourless solid. Yield 57%;

mp 165–167°C; IR (KBr, cm^{-1}) 3300, 3050, 1626, 1600; ^1H NMR (DMSO-d_6) δ 5.24 (s, 4H); 5.28–5.39 (m, 4H); 6.68 (bs, 2H, exchangeable with D_2O); 7.03–8.12 (m, 24H); *m/z* (EI, 70 eV) 554 (M^+, 11), 478 (14), 445 (4), 412 (23), 386 (62), 308 (18), 289 (41), 229 (100), 184 (36), 153 (42). Anal. Calcd For $C_{38}H_{34}O_4$: C, 82.28; H, 6.18. Found: C, 82.14; H, 6.07.

3.1.9. Dibromide 8a. Treatment of diol **7a** (3.324 g, 6 mmol) in CH_2Cl_2 with PBr_3 (0.3 mL, 3 mmol) at 0°C for 6 h followed by usual workup gave the dibromide **8a** as a pale yellow solid. Yield 46%; mp 109°C; IR (KBr, cm^{-1}) 3050, 1626, 1600; ^1H NMR δ 4.47 (m, 4H); 5.02 (s, 4H); 6.22–7.78 (m, 24H); *m/z* (FAB-MS) 684 (M^++ 4); 682 (M^++2); 680 (M^+). Anal. Calcd For $C_{38}H_{32}O_2Br_2$: C, 67.07; H, 4.74. Found: C, 66.89; H, 4.55.

3.1.10. Dibromide 8b. Treatment of diol **8b** (3.324 g, 6 mmol) in CH_2Cl_2 with PBr_3 (0.3 mL, 3 mmol) at 0°C for 6 h followed by usual workup gave the dibromide **8b** as a pale yellow solid. Yield 38%; mp 124°C; IR (KBr, cm^{-1}) 3050, 1626, 1600; ^1H NMR δ 4.56 (m, 4H); 5.13 (s, 4H); 6.18–7.90 (m, 24H); *m/z* (FAB-MS) 684 (M^++ 4); 682 (M^++2); 680 (M^+). Anal. Calcd For $C_{38}H_{32}O_2Br_2$: C, 67.07; H, 4.74. Found: C, 66.76; H, 4.49.

3.1.11. Cyclophane 9a. Dibromide **8a** (0.34 g, 0.5 mmol) and (*S*)-BINOL (0.143 g, 0.5 mmol) were stirred with K_2CO_3 (20 mmol) in acetone (400 mL) at room temperature for 120 h after which the reaction mixture was acidified and evaporated to dryness. The residue obtained was extracted with CH_2Cl_2 (3×100 mL), washed with 10% NaOH (2×50 mL); with water (3×100 mL) and dried ($MgSO_4$). Evaporation of the organic layer gave a residue which was chromatographed over SiO_2 using hexane/$CHCl_3$ (1:1) to afford the chiral cyclophane **9a** as a colourless solid. Yield 21%; mp 191°C; $[\alpha]_D^{25}$=-136.4 (*c* 0.4, $CHCl_3$); IR (KBr, cm^{-1}) 3050, 1632, 1605; ^1H NMR δ 4.81–5.59 (m, 8H); 6.70–6.76 (m, 12H); 7.12–7.37 (m, 16H); 7.75–7.88 (m, 8H); ^{13}C NMR δ 75.1, 84.2, 115.7, 115.7, 115.8, 115.9, 120.7, 123.6, 125.2, 125.9, 126.2, 126.4, 126.5, 126.7, 126.8, 126.8, 126.9, 127.1, 127.1, 127.8, 127.9, 129.1, 129.2, 129.3, 134.2, 136.4, 142.4, 153.9; *m/z* (FAB-MS) 804 (M^+). Anal. Calcd for $C_{58}H_{44}O_4$: C, 86.54; H, 5.51. Found: C, 86.49; H, 5.49.

3.1.12. Cyclophane 9b. Coupling of dibromide **8b** (0.34 g, 0.5 mmol) with (*S*)-BINOL (0.143 g, 0.5 mmol) in the presence of K_2CO_3 (14 g) in acetone (400 mL) at rt for 120 h followed by work up as described above gave a residue, which was purified over SiO_2 using hexane/$CHCl_3$ (1:1) to give the cyclophane **9b** as a colourless solid. Yield 16%; mp 138°C; $[\alpha]_D^{25}$=-120.0 (*c* 0.4, $CHCl_3$); IR (KBr, cm^{-1}) 3050, 1632, 1605; ^1H NMR δ 5.00–5.06 (m, 8H); 6.64 (d, 2H, *J*=8.3 Hz); 6.95 (d, 2H, *J*=8.3 Hz); 7.00–7.56 (m, 24H); 7.76–7.90 (m, 8H); ^{13}C NMR δ 70.4, 114.9, 115.3, 115.9, 117.4, 122.4, 123.2, 123.9, 124.4, 124.9, 125.8, 125.9, 126.4, 127.0, 127.1, 127.4, 127.9, 128.1, 129.4, 129.6, 129.8, 130.9, 134.1, 141.2, 153.3; *m/z* (FAB-MS) 804 (M^+). Anal. Calcd for $C_{58}H_{44}O_{4:}$ C, 86.54; H, 5.51. Found: C, 86.50; H, 5.48.

3.2. UV–visible studies

Complexation studies have been carried out with cyclophane **9a** in (1.83×10^{-3} M) with TCNE (1.99×10^{-3} M) using $CHCl_3/CH_3CN$ (4:1) as solvent. Different solutions were prepared with varying concentrations of TCNE for the same concentration of cyclophane **9a**. The two absorption maxima observed at 416 nm and 398 nm was found to increase with increasing TCNE concentration. Using the Benesi-Hildebrand equation,[7] the association constant (K_a) was found to be 59 M^{-1} from the plot of D_0/[A] against 1/[A]. Similar experiments with cyclophane **9b** and TCNE gave the association constant K_a as 62 M^{-1}.

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