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Dioxastilbenophanes—synthesis and charge transfer complexation studies

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This paper is dedicated to Professor S. Swaminathan (Emeritus Professor, Department of Organic Chemistry, University of Madras, India) on the occasion of his 80th birthday

Abstract—Intramolecular McMurry coupling of dialdehydes derived from xylenyl dibromide and 4-hydroxy benzaldehyde afforded *cis*-stilbenophanes along with cyclophane diols. Stilbenophanes with a large cavity were also synthesized. Charge transfer complexations of the stilbenophanes with TCNE, TCNQ and PQT were studied. Some stilbenophanes form a relatively stronger complex with PQT rather than with TCNE and TCNQ.
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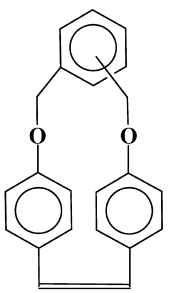
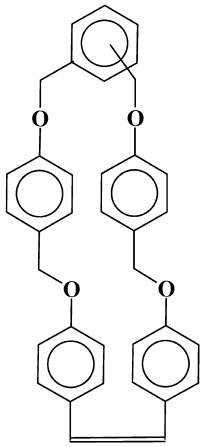
1. Introduction

Non-covalent interactions such as hydrogen bonding, π-stacking, charge-transfer interaction and electrostatic interaction play a pivotal role in supramolecular host–guest complexation.[1] The ability of cyclophanes to include π-electron donors within their cavities as a result of stabilizing noncovalent interactions has led to the construction of a number of mechanically interlocked compounds such as catenanes and rotaxanes.[2] A charge-transfer interaction in a porphyrin–fullerene system was recently studied by Diederich and co-workers.[3] *cis*-and *trans*-stilbene have been the subject of interest from the view-point of structure, property and isomerization.[4] The design and synthesis of cyclophanes possessing rigidly defined cavities and shape-persistent structures of molecular dimensions is of interest to create molecular hosts in the areas of host–guest and electron donor–acceptor complexation.[5] The dimensions of the cavity depend on the spacer group and its connectivity to the arene units. Stilbenophanes are an interesting class of cyclophanes and are synthesized by inter[6] and intramolecular[7] McMurry couplings. During our investigation on the synthesis of various cyclophanes,[8] an attention was focused on introducing the 4,4′-dioxa-*cis*-stilbene unit in the cyclophane skeleton by intramolecular McMurry coupling and then to study the donor–acceptor complexation properties of the resultant host molecules. Stilbenophanes **3a** to **3c** and **8a** to **8c** are classified as electron rich cyclophanes due to the presence of olefin and ether linkages. The electron rich nature of such cyclophanes can be easily proved by their complexation with electron deficient guest molecules like tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ) and 4,4′-dimethylbipyridine hexaflurophosphate (PQT). Hence we report herein the synthesis of stillbenophanes **3a** to **3c** and **8a** to **8c** and their charge transfer complexation studies with electron deficient acceptors.



ortho **3a**
meta **3b**
para **3c**



ortho **8a**
meta **8b**
para **8c**

Keywords: McMurry coupling; Stilbenophane; Charge transfer complexation.

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2. Result and discussion

Treatment of *o*-xylenyl dibromide (**1a**) with 2 equiv. of 4-hydroxybenzaldehyde in DMF in the presence of K_2CO_3 at 70 °C for 48 h afforded the dialdehyde **2a** in 80% yield. Slow addition of 1 equiv. of the dialdehyde **2a** to a solution of 5 equiv. of $TiCl_4$ and 10 equiv. of zinc in THF, followed by refluxing for 24 h resulted in the formation of *cis*-stilbenophanes **3a** (20%) along with cyclophane diol **4a** (60%). It is interesting to note that increasing the concentration of zero valent titanium solution increases the yield of *cis*-stilbenophanes **3a**, **3b** and **3c**. In fact, when the reaction was carried out with 10 equiv. of $TiCl_4$ and 20 equiv. of zinc for 1 equiv. of the dialdehyde **2a**, **2b** and **2c**, stilbenophane **3a**, **3b** and **3c** were obtained in 55, 60 and 53% yield. And the yield of the diols **4a**, **4b** and **4c** decreased. Stilbenophanes **3a**, **3b**, **3c** and stilbenophane diols **4a**, **4b**, **4c** were characterized by spectral and analytical data. From the ^1H NMR, the diol **4a** was found to be a diastereomeric mixture in the ratio 7.5:2.5 (*meso*/DL). Attempts to separate the diastereomeric mixture of the diol **4a** could not be achieved by crystallization and chromatographic techniques. Further, in the present investigation significance was given to the synthesis of cyclophanes rather than the diols. Similarly, other cyclophane diols **4b** and **4c** were also observed as a diastereomeric mixture in the ratio 7:3 and 6.5:3.5 (*meso*/DL) (Scheme 1).

Semi empirical energy minimization calculations using the MOPAC (PM3) method were carried out for *cis* and *trans* isomers of stilbenophane **3c**. The heat of formation of the *cis* isomer of stilbenophane **3c** is 29.5 kcal/mol (Fig. 1a) while that of the *trans* isomer 62.1 kcal/mol (Fig. 1b). Hence the *cis* isomer of **3c** is more stable than the *trans* isomer by a factor of 32.6 kcal/mol. Therefore, the formation of the *cis* isomer is more favoured than the *trans* isomer. The results are in good agreement with the experimental observations. The formation of *cis* stilbenophane **3c** was confirmed based on ^1H NMR. XRD studies also confirmed the structures of **3a** and **3c** as *cis*.[9]

Synthesis of stilbenophanes with large cavities would be more interesting so that a study of the cavity effect on complexation behaviour with electron deficient acceptors like TCNE, TCNQ and PQT could be carried out. With a view to synthesize large cavity stilbenophanes **8a**, **8b** and **8c**, the dialdehydes **2a**, **2b** and **2c**, were reduced with $NaBH_4$ in methanol to give the corresponding diols **5a** to **5c**, which were then converted into corresponding dibromides **6a** to **6c** using PBr_3 in CH_2Cl_2. The dibromides **6a** to **6c** were treated with 2 equiv. of 4-hydroxy benzaldehyde in dry DMF in the presence of K_2CO_3 to obtain the expanded dialdehydes **7a** to **7c**. The expanded dialdehydes **7a** to **7c** were subjected to intramolecular McMurry coupling by slow addition (16 h) of the dialdehyde **7a** to **7c** to a mixture of $TiCl_4$ (10 equiv.) and Zn (20 equiv.) for 1 equiv. of dialdehyde in THF, followed by reflux (24 h) to give the *cis* stilbenophane **8a** to **8c** (Scheme 2).

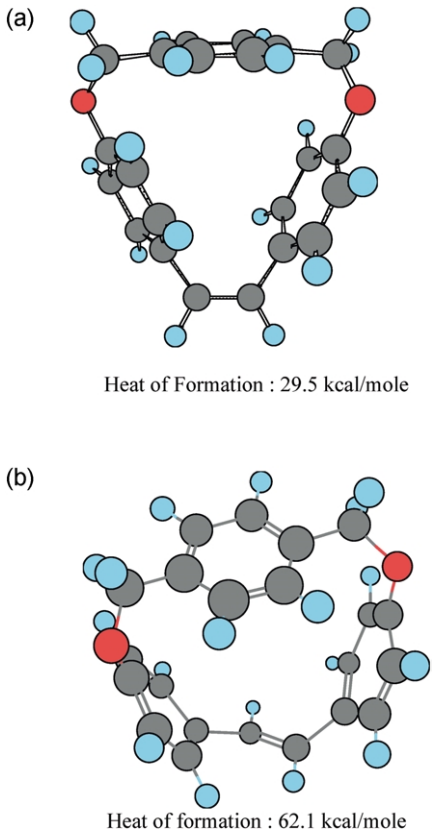
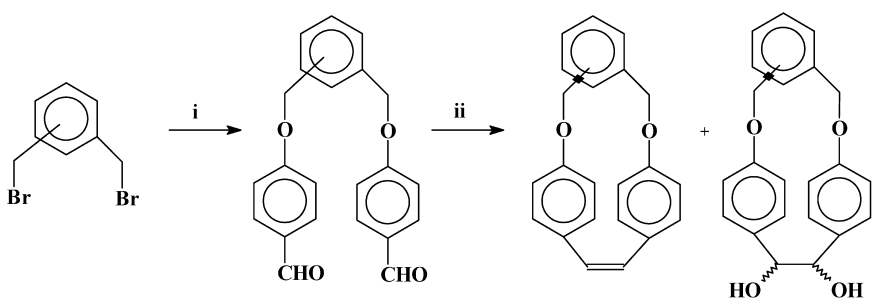
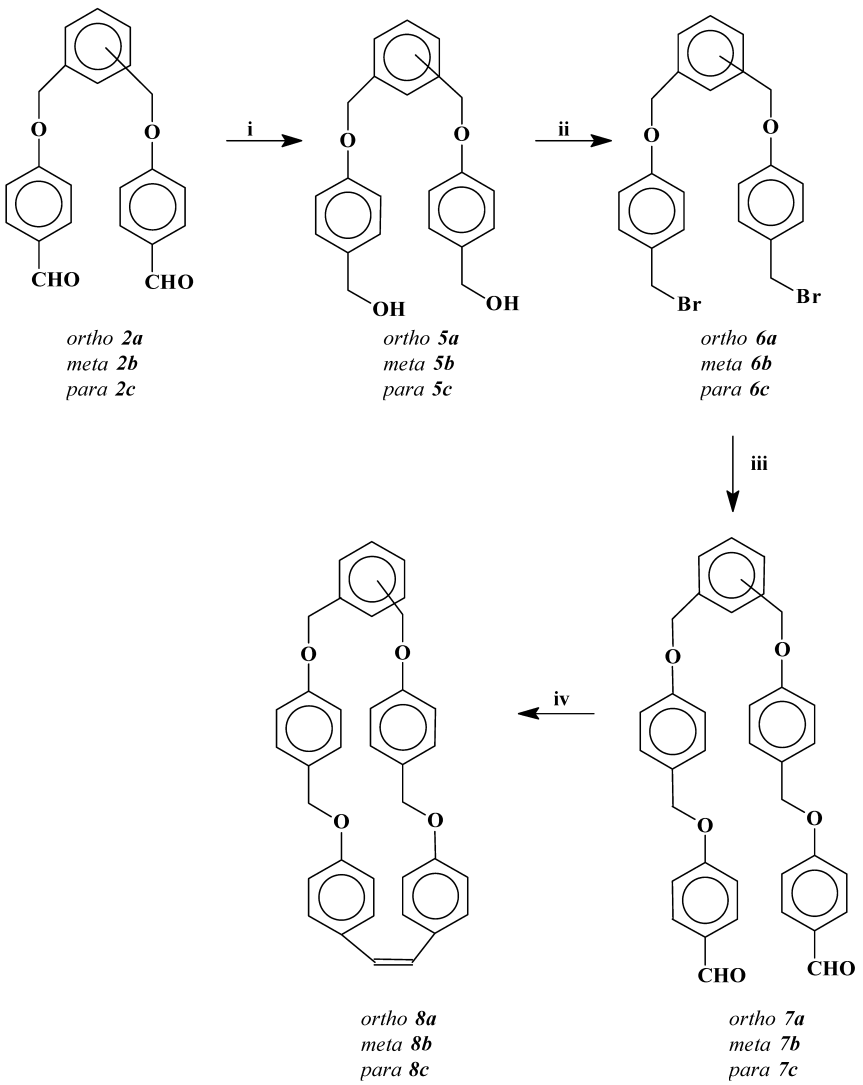


Figure 1. (a) Heat of Formation of *cis* isomer of stilbenophane **3c**: 29.5 kcal/mol. (b) Heat of formation *trans* isomer of stilbenophane **3c**: 62.1 kcal/mol.



ortho ***1a*** *meta* ***1b*** *para* ***1c*** — *ortho* ***2a*** *meta* ***2b*** *para* ***2c*** — *ortho* ***3a*** *meta* ***3b*** *para* ***3c*** — *ortho* ***4a*** *meta* ***4b*** *para* ***4c***

Scheme 1. (i) 4-Hydroxy benzaldehyde (2 equiv.), K_2CO_3, DMF, 70 °C, 48 h, (ii) $TiCl_4$ (5 equiv.), Zn (10 equiv.) for dialdehyde (1 equiv.), THF, slow addition 16 h, reflux 24 h or $TiCl_4$ (10 equiv.), Zn (20 equiv.) for dialdehyde (1 equiv.), THF, slow addition 16 h, reflux 24 h.



Scheme 2. (i) $NaBH_4$, MeOH, 12 h, (ii) PBr_3, CH_2Cl_2, 12 h, (iii) 4-hydroxybenzaldehyde (2 equiv.), K_2CO_3, DMF, 70 °C, 2 days, (iv) $TiCl_4$ (10 equiv.), Zn (20 equiv.), THF, slow addition 16 h, reflux 24 h.

3. Complexation studies

Stilbenophanes **3a**, **3b** and **3c** show UV–Vis absorption maxima at 238.8, 239.4 and 235.6 nm, respectively, in the solvent medium CH_3CN/CH_2Cl_2 (4:1). However, the acceptor TCNE, TCNQ and PQT show absorption maxima at 286.8, 274.0 and 263.0 nm, respectively, in the same solvent mixture. Stilbenophanes **3a**, **3b** and **3c** forms a charge transfer complex with TCNE as evidenced by the appearance of absorption maxima at 394.0, 414.6 and 473.0 nm, respectively. The equilibrium constant for charge transfer complexation of **3a** with TCNE was observed at 473 nm (Fig. 2 CT behaviour of **3a** with TCNE). Similarly stilbenophanes **3a**, **3b** and **3c** form charge transfer complexes with TCNQ as indicated by absorption at 665.0 and 760.0 nm apart from 743.0 nm (Fig. 3 CT behaviour of **3a** with TCNQ). Stilbenophanes **3a**, **3b** and **3c** with PQT shows charge transfer absorption maxima only at 394.0 nm (Fig. 4 CT behaviour of **3a** with PQT).

From the plot of the D_0/A vs $1/A_0$ and by the Benesi–Hildebrand equation[10] the stability constant of the charge transfer complex of stilbenophanes **3a** to **3c** with various

Table 1. Stability constant for the charge transfer complex of **3a** to **3c** with acceptors TCNE, TCNQ and PQT

cis-Stilbenophane	TCNE (473 nm)		TCNQ (743 nm)		PQT (394 nm)	
	K_C^{AD}	ϵ^{AD}	K_C^{AD}	ϵ^{AD}	K_C^{AD}	ϵ^{AD}
3a	20	1.3×10^4	130	4.5×10^3	200	1.0×10^3
3b	30	1.7×10^4	300	3.3×10^3	100	5.0×10^3
3c	100	2.5×10^4	100	1.0×10^3	1667	1.0×10^5

Table 2. Stability constant for the charge transfer complex of **8c** with acceptors TCNE, TCNQ and PQT

Cyclophane	TCNE (474 nm)		TCNQ (761 nm)		PQT (395.2 nm)	
	K_C^{AD}	ϵ^{AD}	K_C^{AD}	ϵ^{AD}	K_C^{AD}	ϵ^{AD}
8c	20	5.0×10^4	142.8	1.0×10^4	2000	2.5×10^4

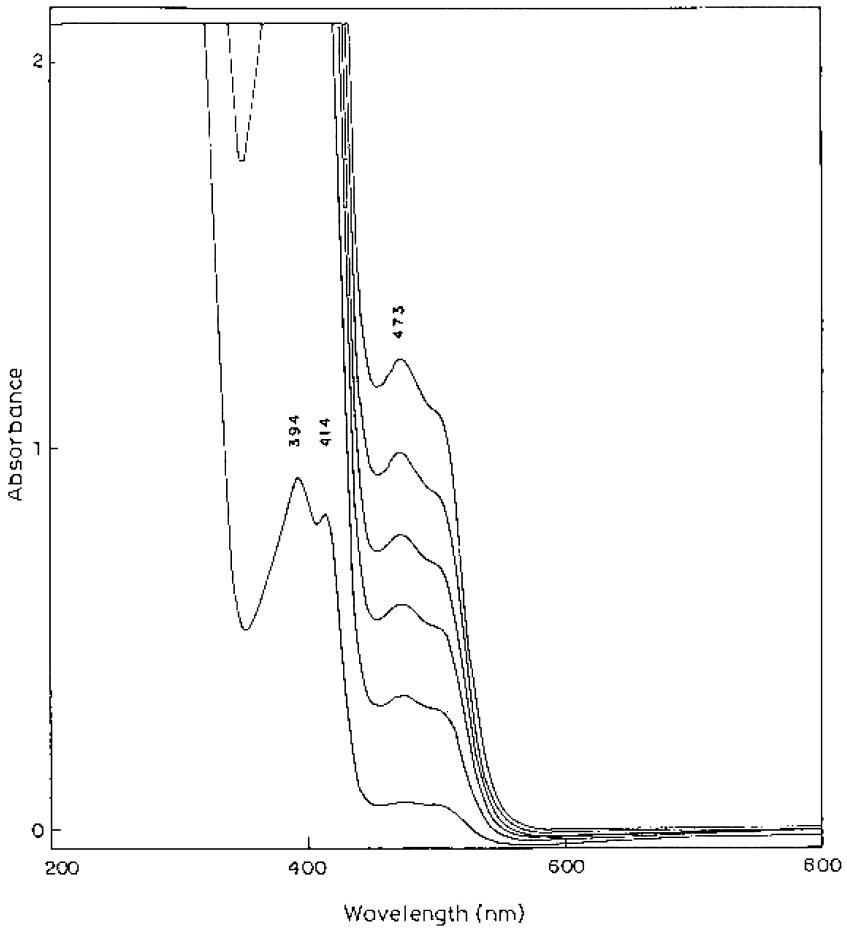


Figure 2. Charge transfer complexation behaviour of stilbenophane **3a** with TCNE.

acceptors TCNE, TCNQ and PQT were determined (Table 1).

It is noteworthy that stilbenophane **3c** forms a strong charge transfer complex with PQT ($K_c^{AD,}$ 1667 M^{-1}; ϵ^{AD}, 1.0×10^5).

The ability of stilbenophane **8c** to form charge transfer complex with electron deficient acceptors like TCNE, TCNQ and PQT was then explored. Table 2 shows the K_c values for the charge transfer complex of **8c** with TCNE, TCNQ and PQT.

Comparing the stability constants values of **3a**, **3b**, **3c** with **8c**, it was found that the stability constant values are relatively similar and hence the cavity size does not have very high influence on the stability of charge transfer complexes. Though K_c for the complex derived from **8c** with PQT is slightly on the higher side when compared with the complex derived from **3c** with PQT, the results are comparable within experimental errors. Similarly the stability constants values of **8a** and **8b** with TCNE, TCNQ and PQT are comparable with that of **3a** and **3b**.

In conclusion, we have synthesized a new class of electron rich cyclophanes (**3a** to **3c**, and **8a** to **8c**) possessing a 4,4′-dioxa-*cis*-stilbene unit and studied their CT complexation ability with electron poor guest molecules like TCNE, TCNQ and PQT. It was interesting to note that the cyclophanes **3c** and **8c** form a strong CT complex with PQT due to electronic complementary matching between donor and acceptor.

4. Experimental

All the melting points are uncorrected. The IR spectra were recorded using Shimadzu FT-IR 8300 instrument. The ^1H and ^{13}C NMR spectra of all compounds in $CDCl_3$ were recorded using Jeol GSX 400 (400 MHz) NMR spectrometer. The mass spectra were recorded using Jeol (EI, 70 eV and FAB-MS). The column chromatography was performed using silica gel (100–200 mesh).

4.1. General procedure for O-alkylation (procedure A)

A mixture of *p*-hydroxybenzaldehyde (21 mmol), the dibromide **1a/1b/1c** (10 mmol) and potassium carbonate (15 g) in anhydrous DMF (60 mL) was stirred under nitrogen for 48 h at 60 °C. The reaction mixture was poured into water (2 L) and stirred. The resulting precipitate was filtered, washed with water (3×150 mL) and dissolved in CH_2Cl_2 (350 mL). The organic layer was washed with NaOH solution (5% w/v, 2×100 mL), dried (Na_2SO_4) and evaporated to give a residue, which was chromatographed (SiO_2) using hexane/$CHCl_3$ (1:2) to give the corresponding dialdehyde **2a/2b/2c**.

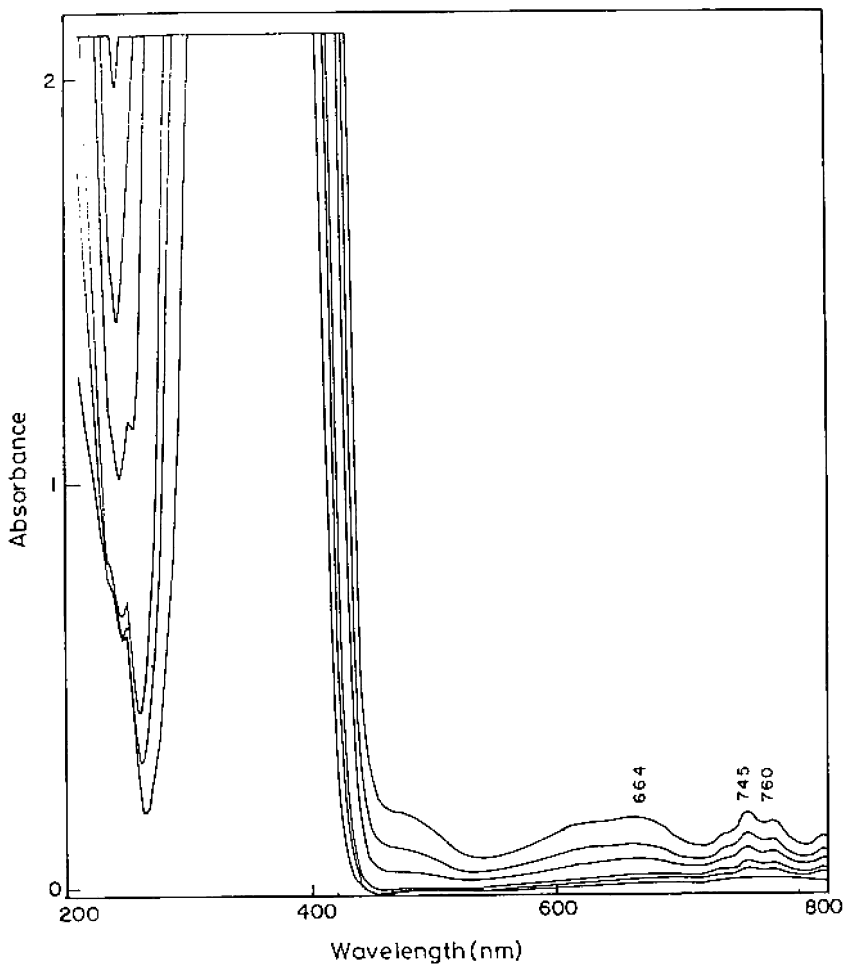


Figure 3. Charge transfer complexation behaviour of stilbenophane **3a** with TCNQ.

4.1.1. Dialdehyde 2a. Following the general procedure A, the dialdehyde **2a** was obtained as a white solid from *o*-xylenyl dibromide (**1a**).

Yield: 80%. Mp: 126 °C. IR: (KBr, cm^{-1}) 1687 (C=O). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ=5.18 (s, 4H, Ar-CH_2O), 6.94 [d, $^3J_{H,H}$=7.2 Hz, 4H, Ar-H], 7.32–7.45 (m, 4H, Ar-H), 7.73 [d, $^3J_{H,H}$=7.2 Hz, 4H, Ar-H], 9.79 (s, 2H, CHO). ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ=71.3, 114.9, 125.7, 126.8, 128.3, 130.6, 134.7, 162.5, 190.9. Mass spectrum: *m/z* (EI, 70 eV) 346 (M^+). Elemental analysis calcd for $C_{22}H_{18}O_4$: C, 76.30; H, 5.20; found, C, 76.14; H, 5.08.

4.1.2. Dialdehyde 2b. Following the general procedure A, the dialdehyde **2b** was obtained as a white solid from *m*-xylenyl dibromide (**1b**).

Yield: 86%. Mp: 163 °C. IR: (KBr, cm^{-1}) 1681 (C=O). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ=5.17 (s, 4H, Ar-CH_2O), 7.07 [d, $^3J_{H,H}$=7.2 Hz, 4H, Ar-H], 7.43–7.45 (m, 3H, Ar-H), 7.51 (s, 1H, Ar-H), 7.84 [d, $^3J_{H,H}$=7.2 Hz, 4H, Ar-H], 9.88 (s, 2H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=70.2, 115.3, 126.6, 127.5, 129.3, 130.4, 132.2, 136.8, 163.7, 190.9. Mass spectrum: *m/z* (EI, 70 eV) 346 (M^+). Elemental analysis calcd for $C_{22}H_{18}O_4$: C, 76.30; H, 5.20; found, C, 76.21; H, 5.11.

4.1.3. Dialdehyde 2c. Following the general procedure A, the dialdehyde **2c** was obtained as a white solid from *p*-xylenyl dibromide (**1c**).

Yield: 86%. Mp: 110 °C. IR (KBr, cm^{-1}): 1684 (C=O). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ=5.13 (s, 4H, Ar-CH_2O), 6.96 [d, $^3J_{H,H}$=7.2 Hz, 4H, Ar-H], 7.44 (m, 4H, Ar-H), 7.84 [d, $^3J_{H,H}$=7.2 Hz, 4H, Ar-H], 9.81 (s, 2H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=71.8, 115.1, 123.7, 126.3, 129.1, 132.4, 161.4, 190.9. Mass spectrum: *m/z* (EI, 70 eV) 346 (M^+). Elemental analysis calcd for $C_{22}H_{18}O_4$: C, 76.30; H, 5.20; found, C, 76.11; H, 5.12.

4.2. General procedure for intramolecular McMurry coupling (procedure B)

A solution of zero valent titanium [Ti(0)] prepared from $TiCl_4$ (7.23 mmol, 5 equiv.) with zinc (14.5 mmol, 10 equiv.) in dry THF (300 mL) under a nitrogen atmosphere at 0 °C and was allowed to attain room temperature after 0.5 h and then refluxed for 1 h. A solution of the dialdehyde (1.45 mmol, 1 equiv.) in THF (100 mL) was slowly added at reflux to the freshly prepared zero valent titanium during a period of 16 h. After the addition was over, the reaction mixture was refluxed for 24 h. The reaction mixture was then quenched with saturated K_2CO_3

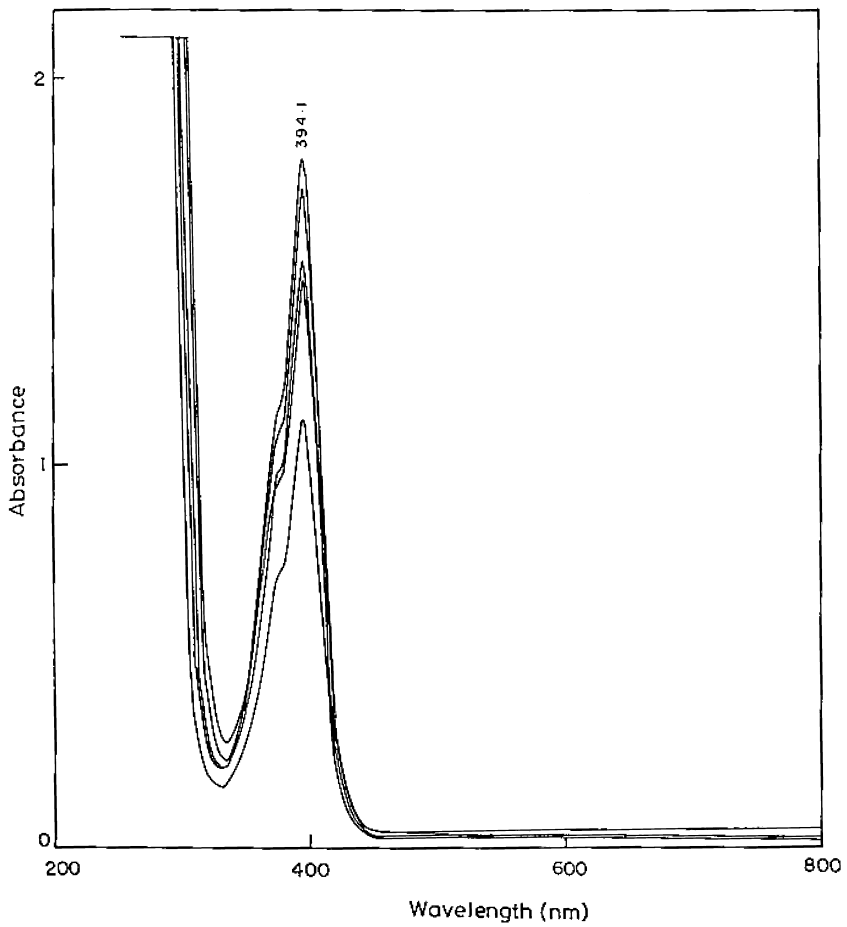


Figure 4. Charge transfer complexation behaviour of stilbenophane **3a** with PQT.

solution. The precipitated inorganic material was removed by filteration. The precipitate was thoroughly washed with THF (100 mL) and the THF extract was evaporated to give a residue which was then dissolved in $CHCl_3$ (200 mL), washed with water (2×200 mL), brine (100 mL) and dried over Na_2SO_4. Crude product obtained after evaporation of $CHCl_3$, was purified by column chromatography. Elution with hexane/$CHCl_3$ (8:2) afforded the stilbenophanes and further elution with hexane/$CHCl_3$ (2:8) gave the stilbene diols.

4.3. Modified procedure for the preparation of stilbenophanes (procedure C)

A solution of zero valent titanium [Ti(0)] prepared from $TiCl_4$ (14.5 mmol, 10 equiv.) with zinc (29 mmol, 10 equiv.) in dry THF (300 mL) under a nitrogen atmosphere at 0 °C and was allowed to attain room temperature after 0.5 h and then refluxed for 1 h. A solution of dialdehyde (1.45 mmol, 1 equiv.) in THF (100 mL) was added slowly at reflux to the freshly prepared zero valent titanium solution and the experiment was carried out and worked up as mentioned in the procedure B to give the stilbenophanes as the major product.

4.3.1. *cis*-Stilbenophane 3a. Following the general procedure B/C, the dialdehyde **2a** was subjected to intramolecular McMurry coupling to give the cyclophane **3a**.

Yield: 20% (procedure B) and 55% (procedure C). White solid, Mp: 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=4.82 (s, 4H, Ar-CH_2O), 6.42 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 6.49 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 7.02 (s, 2H, stilbenic), 7.37 [dd, $^3J_{H,H}$=5.9, 2.4 Hz, 2H, Ar-H], ^{13}C NMR (100.3 MHz, $CDCl_3$, 25 °C): δ=70.9, 120.1, 127.6, 129.6, 131.0, 134.5, 135.4, 135.8, 157.4. Mass spectrum: *m/z* (EI, 70 eV) 314 (M^+). Elemental analysis calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73; found, C, 83.96; H, 5.64.

4.3.2. *cis*-Stilbenophane 3b. Following the general procedure B/C, the dialdehyde **2b** was subjected to intramolecular McMurry coupling to give the cyclophane **3b**.

Yield: 20% (procedure B); and 60% (procedure C). White solid, Mp: 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=4.96 (s, 4H, Ar-CH_2O), 6.42 [d, $^3J_{H,H}$=8.8 Hz, 4H], 6.50 [d, $^3J_{H,H}$=8.3 Hz, 4H], 6.89 (s, 2H, stilbenic), 7.19–7.31 (m, 4H, Ar-H). ^{13}C NMR (100.3 MHz, $CDCl_3$, 25 °C): δ=71.5, 117.3, 128.7, 128.9, 130.3, 130.4, 132.3, 134.2, 136.5, 155.2. Mass spectrum: *m/z* (EI, 70 eV) 314 (M^+). Elemental analysis calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73; found, C, 83.93; H, 5.59.

4.3.3. *cis*-Stilbenophane 3c. Following the general procedure B/C, the dialdehyde **2c** was subjected to intramolecular McMurry coupling to give the cyclophane **3c**.

Yield: 20% (procedure B); and 53% (procedure C). White solid, Mp: 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.09 (s, 4H, Ar-CH_2O), 6.34 [d, $^3J_{H,H}$=6.8 Hz, 4H], 6.43 [d, $^3J_{H,H}$=6.4 Hz, 4H], 6.68 (s, 2H, stilbenic); 7.06 (s, 4H, Ar-H). ^{13}C NMR (100.3 MHz, $CDCl_3$): δ=69.9, 116.8, 129.4, 129.5, 130.9, 133.2, 136.3, 154.6. Mass spectrum: *m/z* (EI, 70 eV) 314 (M^+). Elemental analysis calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73; found, C, 83.98; H, 5.65.

4.3.4. Cyclophane diol 4a. Following the general procedure B, the dialdehyde **2a** was subjected to intramolecular McMurry coupling to give the diol **4a**.

Yield: 60%. White solid, Mp: 201 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ=4.85 (s, 4H, Ar-CH_2O), 5.12 (s, 2H, Ar-C*H*–OH), 6.12–6.36 (m, 6H, Ar-H), 6.86 [d, $^3J_{H,H}$=7.8 Hz, 2H, Ar-H], 7.38 [dd, 2H, $^3J_{H,H}$=6.8, 2.6 Hz, Ar-H], 7.48 (s, 2H, exchanged with D_2O, OH); 7.72 [dd, $^3J_{H,H}$=6.6, 2.7 Hz, 2H]. ^{13}C NMR (100.3 MHz, DMSO-d_6, 25 °C): δ=69.7, 74.1, 118.6, 119.4, 126.4, 127.2, 129.4, 135.5, 157.3. Mass spectrum: *m/z* (EI, 70 eV) 348 (M^+). Elemental analysis calcd for $C_{22}H_{20}O_4$: C, 75.86; H, 5.75; found, C, 75.67; H, 5.53.

4.3.5. Cyclophane diol 4b. Following the general procedure B, the dialdehyde **2b** was subjected to intramolecular McMurry coupling to give the diol **4b**.

Yield: 56%. White solid, Mp: 185 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ=5.07 (s, 4H, Ar-CH_2O), 5.41 (s, 2H, Ar-CHOH), 6.26–6.58 (m, 8H, Ar-H), 6.86 (s, 2H, exchanged with D_2O, OH), 7.26–7.38 (m, 4H, Ar-H). ^{13}C NMR (100.3 MHz, DMSO-d_6, 25 °C): δ=68.9, 80.01, 114.1, 116.9, 126.5, 127.9, 128.7, 135.0, 136.9, 155.2. Mass spectrum: *m/z* (EI, 70 eV) 348 (M^+). Elemental analysis calcd for $C_{22}H_{20}O_4$: C, 75.86; H, 5.75; found, C, 75.77; H, 5.65.

4.3.6. Cyclophane diol 4c. Following the general procedure B, the dialdehyde **2c** was subjected to intramolecular McMurry coupling to give the diol **4c**.

Yield: 62%. White solid, Mp: 212 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ=5.09 (s, 4H, Ar-CH_2O), 5.35 (s, 2H, Ar-CHOH), 6.88–7.22 (m, 8H, Ar-H), 7.41 (s, 2H, exchanged with D_2O, OH), 7.68 (s, 4H, Ar-H). ^{13}C NMR (100.3 MHz, DMSO-d_6, 25 °C): δ=65.9, 78.4, 125.2, 127.5, 129.6, 135.3, 141.1, 152.5. Mass spectrum: *m/z* (EI, 70 eV) 348 (M^+). Elemental analysis calcd for $C_{22}H_{20}O_4$: C, 75.86; H, 5.75; found, C, 75.71; H, 5.63.

4.4. General procedure for the reduction of dialdehyde with $NaBH_4$ (procedure D)

To a solution of the dialdehyde **2a/2b/2c** (8 mmol) in methanol (70 mL) was added $NaBH_4$ (4 mmol) in portions 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 **5a/5b/5c**, which was purified by recrystallization from $CHCl_3$/MeOH (5:1).

4.4.1. Diol 5a. Following the general procedure D, the diol **5a** was obtained from the dialdehyde **2a**.

Yield: 90%. White solid, Mp: 196 °C. IR: (KBr, cm^{-1}) 3280 (b, OH). ^{1}H NMR (90 MHz, DMSO-d_6, 25 °C) δ=4.48 (s, 4H, Ar-CH_2OH), 5.12 (s, 4H, Ar-CH_2O), 6.35 (bs, 2H, exchangeable with D_2O), 7.02 (d, $^3J_{H,H}$=7.4 Hz, 4H, Ar-H), 7.22–7.49 (m, 4H, Ar-H); 7.53 (d, $^3J_{H,H}$=7.6 Hz, 4H, Ar-H). Mass spectrum: *m/z* (EI, 70 eV) 350 (M^+). Elemental analysis calcd for $C_{22}H_{22}O_4$: C, 75.43; H, 6.29; found, C, 75.22; H, 6.15.

4.4.2. Diol 5a. Following the general procedure D, the diol **5b** was obtained from the dialdehyde **2b**.

Yield: 95%. White solid, Mp: 211 °C. IR: (KBr, cm^{-1}) 3300 (b, OH); ^{1}H NMR: (90 MHz, DMSO-d_6, 25 °C) δ=4.53 (s, 4H, Ar-CH_2OH), 5.14 (s, 4H, Ar-CH_2O), 6.46 (bs, 2H, exchangeable with D_2O, OH); 7.07 [d, $^3J_{H,H}$=7.8 Hz, 4H, Ar-H], 7.24–7.47 (m, 4H, Ar-H); 7.53 [d, $^3J_{H,H}$=7.8 Hz, 4H, Ar-H]. Mass spectrum: *m/z* (EI, 70 eV) 350 (M^+). Elemental analysis calcd for $C_{22}H_{22}O_4$: C, 75.43; H, 6.29; found, C, 75.32; H, 6.08.

4.4.3. Diol 5c. Following the general procedure D, the diol **5c** was obtained from the dialdehyde **2c**.

Yield: 85%. White solid, Mp: 205 °C. IR: (KBr, cm^{-1}) 3320 (b, OH). ^{1}H NMR (90 MHz, DMSO-d_6, 25 °C) δ=4.48 (s, 4H, Ar-CH_2OH), 5.11 (s, 4H, Ar-CH_2O), 6.38 (bs, 2H, exchangeable with D_2O, OH), 6.99 [d, $^3J_{H,H}$=7.7 Hz, 4H, Ar-H], 7.43 (s, 4H, Ar-H), 7.52 [d, $^3J_{H,H}$=7.5 Hz, 4H, Ar-H]. Mass spectrum: *m/z* (EI, 70 eV) 350 (M^+). Elemental analysis calcd for $C_{22}H_{22}O_4$: C, 75.43; H, 6.29; found, C, 75.24; H, 6.18.

4.5. General procedure for the conversion of the diol into the dibromide (procedure E)

To a stirred suspension of the diol **5a/5b/5c** (6 mmol) in CH_2Cl_2 (120 mL), PBr_3 (3 mmol) was added and the reaction mixture was stirred at 0 °C for 12 h. The reaction mixture was poured into water (500 mL) and the organic layer was rapidly washed with water (3×150 mL) followed by brine (200 mL) and dried. The solvent was evaporated in vacuo to give dibromide **6a/6b/6c**, which was purified by recrystallization from hexane/CH_2Cl_2 (1:5).

4.5.1. Dibromide 6a. Following the general procedure E, the dibromide **6a** was obtained from the diol **5a**.

Yield: 75%. White solid, Mp: 134 °C. ^{1}H NMR (90 MHz, $CDCl_3$, 25 °C): δ=4.51 (s, 4H, Ar-CH_2Br), 5.04 (s, 4H, Ar-CH_2O), 6.97 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 7.15–7.29 (m, 4H, Ar-H); 7.37 [d, 4H, $^3J_{H,H}$=8.8 Hz, Ar-H]. Mass spectrum: *m/z* (EI, 70 eV) 476 (M^+).

4.5.2. Dibromide 6b. Following the general procedure E, the dibromide **6a** was obtained from the diol **5b**.

Yield: 87%. White solid, Mp: 146 °C. ^{1}H NMR (90 MHz, $CDCl_3$, 25 °C): δ=4.57 (s, 4H, Ar-CH_2Br), 5.13 (s, 4H, Ar-CH_2O), 7.00 [d, 4H, $^3J_{H,H}$=8.8 Hz, Ar-H], 7.24–7.32 (m, 4H, Ar-H), 7.39 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H]. Mass spectrum: *m/z* (EI, 70 eV) 476 (M^+).

4.5.3. Dibromide 6c. Following the general procedure E, the dibromide **6c** was obtained from the diol **5c**.

Yield: 72%. White solid, Mp: 135 °C. ^{1}H NMR (90 MHz, $CDCl_3$, 25 °C): δ=4.54 (s, 4H, Ar-CH_2Br), 5.09 (s, 4H, Ar-CH_2O), 6.94 (d, 4H, $^3J_{H,H}$=8.4 Hz), 7.32 (s, 4H), 7.39 (d, 4H, $^3J_{H,H}$=8.8 Hz). Mass spectrum: *m/z* (EI, 70 eV) 476 (M^+).

4.5.4. Dialdehyde 7a. Following the general procedure A, the dialdehyde **7a** was obtained from dibromide **6a** and *p*-hydroxy benzaldehyde.

Yield: 70%. White solid, Mp: 156 °C. IR: (KBr, cm^{-1}) 1682 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.07 (s, 4H, Ar-CH_2O); 5.09 (s, 4H, Ar-CH_2O); 7.00 [d, $^3J_{H,H}$=8.3 Hz, 4H], 7.06 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 7.36 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.41 (s, 4H, Ar-H), 7.83 [d, $^3J_{H,H}$=8.3 Hz, 4H], 9.88 (s, 2H, CHO). ^{13}C NMR (100.3 MHz, $CDCl_3$, 25 °C): δ=69.8, 70.0, 115.0, 115.1, 126.4, 127.1, 128.9, 129.3, 129.9, 131.9, 137.2, 158.8, 163.8, 190.8. Mass spectrum: *m/z* (EI, 70 eV) 558 (M^+). Elemental analysis calcd for $C_{36}H_{30}O_6$: C, 77.42; H, 5.38; found, C, 77.25; H, 5.16.

4.5.5. Dialdehyde 7b. Following the general procedure A, the dialdehyde **7b** was obtained from dibromide **6b** and *p*-hydroxy benzaldehyde.

Yield: 65%. White solid, Mp: 143 °C. IR: (KBr, cm^{-1}) 1686 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.06 (s, 4H, Ar-CH_2O), 5.18 (s, 4H, Ar-CH_2O), 6.99 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.05 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.25 (s, 1H, Ar-H), 7.35 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.36–7.53 (m, 3H, Ar-H), 7.83 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 9.88 (s, 2H, CHO). ^{13}C NMR (100.3 MHz, $CDCl_3$, 25 °C): δ=68.0, 69.9, 114.9, 115.1, 128.4, 128.5, 129.0, 129.3, 130.0, 131.9, 134.9, 158.7, 163.7, 190.8. Mass spectrum: *m/z* (EI, 70 eV) 558 (M^+). Elemental analysis calcd for $C_{36}H_{30}O_6$: C, 77.42; H, 5.38; found, C, 77.31; H, 5.26.

4.5.6. Dialdehyde 7c. Following the general procedure A, the dialdehyde **7c** was obtained from dibromide **6c** and *p*-hydroxy benzaldehyde.

Yield: 72%. White solid, Mp: 154 °C. IR: (KBr, cm^{-1}) 1687 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.02 (s, 4H, Ar-CH_2O), 5.10 (s, 4H, Ar-CH_2O), 6.92 [d, *J*=8.8 Hz, 4H]; 7.28 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 7.45 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.76 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 7.95 (s, 4H, Ar-H), 9.81 (s, 2H, CHO). ^{13}C NMR (100.3 MHz, $CDCl_3$, 25 °C): δ=68.1, 69.7, 115.0, 127.6, 128.2, 128.8, 129.3, 130.9, 132.0, 132.4, 162.6, 166.8, 190.8. Mass spectrum: *m/z* (EI, 70 eV) 558 (M^+). Elemental analysis calcd for $C_{36}H_{30}O_6$: C, 77.42; H, 5.38; found, C, 77.27; H, 5.23.

4.5.7. Cyclophane 8a. Following the general procedure C, the dialdehyde **7a** was subjected to intramolecular McMurry coupling to give the cyclophane **8a**.

Yield: 25%. White solid, Mp: 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.06 (s, 8H, Ar-CH_2O), 6.72 [d, $^3J_{H,H}$=8.3 Hz, 8H, Ar-H], 6.81 (s, 2H, stilbenic), 7.38 [d, 8H, $^3J_{H,H}$=8.5 Hz, 8H, Ar-H], 7.85 (s, 4H, Ar-H). ^{13}C NMR (100.4 MHz, $CDCl_3$, 25 °C): δ=69.3, 69.9, 114.9, 115.3, 121.4, 123.6, 126.8, 128.3, 129.7, 130.6, 131.4, 136.4, 157.2, 162.5. Mass spectrum: *m/z* (EI, 70 eV) 526 (M^+). Elemental analysis calcd for $C_{36}H_{30}O_4$: C, 82.13; H, 5.70; found, C, 82.08; H, 5.58.

4.5.8. Cyclophane 8b. Following the general procedure C, the dialdehyde **7b** was subjected to intramolecular McMurry coupling to give the cyclophane **8b**.

Yield: 30%. White solid, Mp: 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.05 (s, 8H, Ar-CH_2O), 6.78 [d, $^3J_{H,H}$=8.3 Hz, 8H, Ar-H], 6.98 (s, 2H, stilbenic), 7.46 [d, $^3J_{H,H}$=8.3 Hz, 8H, Ar-H], 7.64–7.67 (m, 4H, Ar-H). ^{13}C NMR (100.3 MHz, $CDCl_3$, 25 °C): δ=68.4, 70.2, 115.1, 115.5, 116.2, 119.3, 127.5, 128.1, 129.2, 129.7, 130.2, 131.7, 133.8, 156.7, 162.3. Mass spectrum: *m/z* (EI, 70 eV) 526 (M^+). Elemental analysis calcd for $C_{36}H_{30}O_4$: C, 82.13; H, 5.70; found, C, 82.08; H, 5.61.

4.5.9. Cyclophane 8c. Following the general procedure C, the dialdehyde **7c** was subjected to intramolecular McMurry coupling to give the cyclophane **8c**.

Yield: 35%. White solid, Mp: 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=5.09 (s, 8H, Ar-CH_2O), 6.94 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.25 [d, *J*=8.3 Hz, 4H, Ar-H], 7.31 (s, 2H, stilbenic), 7.38 [d, $^3J_{H,H}$=8.8 Hz, 4H, Ar-H], 7.68 [d, $^3J_{H,H}$=8.3 Hz, 4H, Ar-H], 7.95 (s, 4H, Ar-H). ^{13}C NMR:(100.3 MHz, $CDCl_3$, 25 °C) δ=68.3, 69.5, 115.2, 126.7, 127.2, 128.5, 120.8, 131.4, 132.3, 133.6, 144.6, 163.5, 167.3. Mass spectrum: *m/z* (EI, 70 eV) 526 (M^+). Elemental analysis calcd for $C_{36}H_{30}O_4$: C, 82.13; H, 5.70; found, C, 82.08; H, 5.59.

4.6. Complexation studies

Charge transfer complexation studies were carried out by preparing 1×10^{-5} M solution of stilbenophane **3a** to **3c**, **8c** with gradual addition of acceptor (2 mg) in a 4:1 mixture of CH_3CN and CH_2Cl_2. (10 mL). Gradual addition of TCNE with stilbenophanes **3a** to **3c** rapidly increases the intensity of charge transfer bands at 394.0 and 414.6 nm. Hence the equilibrium constant was measured at 473.0 nm only. The equilibrium constant for the CT complex derived from the **3a**, **3b** and **3c** with TCNQ was measured at 743 nm though absorption bands were observed at 665 and 760 nm. Similarly, the equilibrium constant for the charge transfer complex derived from **3a**, **3b** and **3c** with PQT was measured at 394 nm. Absorbance is measured at a suitable wavelength as mentioned above with change in the concentration of the acceptor in term of 2 mg with concentration of the stilbenophane receptor being kept constant. Plot of D_0/A (D_0 is the concentration of stilbenophane and A is the concentration of acceptor) vs $1/A_0$ (A_0 is the absorbance of the complex at charge transfer

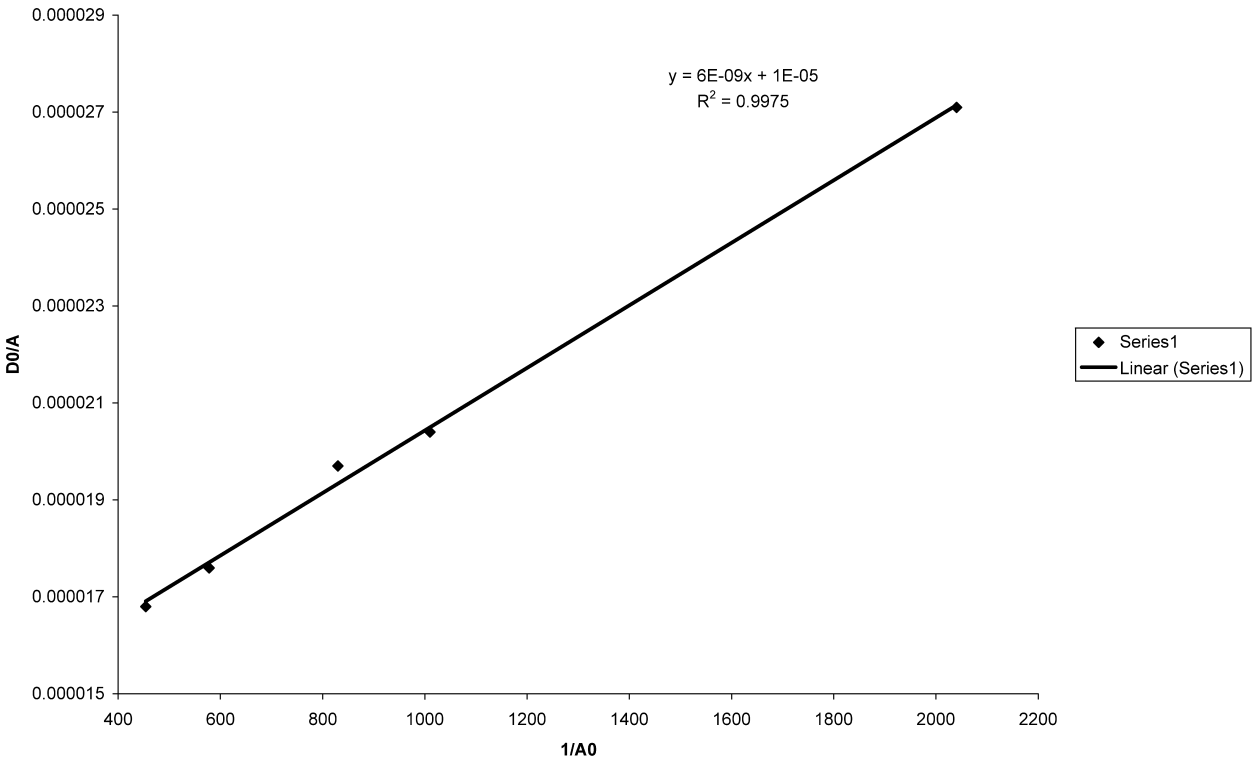


Figure 5. Plot of D0/A versus 1/A0 for determination of stability constant (e.g. stilbenophane 3c with PQT).

transition) gave a straight line indicating the stoichiometry of the complex as 1:1 (Fig. 5 plot of D_0/A vs $1/A_0$ for the complex of **3c** with PQT). By applying the Benesi–Hildebrand equation, the reciprocal of the intercept on the *Y*-axis provided the information about ϵ^{AD} (ϵ of donor–acceptor complex) and from the slope of the line, K_c^{AD} (equilibrium constant of the donor acceptor complex) was calculated. Similarly K_c^{AD} for the charge transfer complex of **8c** with PQT was also determined. Thus by making use of UV–Visible spectroscopy, the stability constant of charge transfer complexes of stilbenophane **3a** to **3c** and **8c** with various acceptors TCNE, TCNQ and PQT were determined.

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