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Benzotriazolophanes—New Class of Novel Cyclophanes

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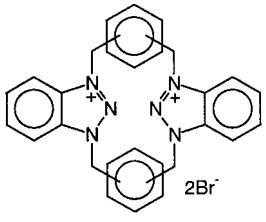
Abstract—Alkylation of benzotriazole with various xylenyl dibromides (*o*, *m*, *p*) or 4,4′-bis(bromethyl)biphenyl in two steps afforded the benzotriazolophanes **2** or **3**. Similarly alkylation of benzotriazole with 4,4″-bis(bromomethyl)-1,1′:3′,1″-terphenyl in two steps gave the unprecedented benzotriazolophane **4a**. By similar alkylation procedure, cyclophanes **4b**, **4c** and **4d** were obtained from the substituted dibromides **6b**, **6c** and **6d,** respectively. Novel cross-linked benzotriazolophane **5** was obtained by using the tetrabromide **9** as the spacer unit.

Introduction

Cyclophanes with a heterocyclic ring system possesses a favorable binding site for metal ions[1] and hence can have promising properties[2] as molecular hosts. Synthesis of Pyridinophanes,[3] Ureaphanes[4] and Imidazolophanes[5] has been recently reported. Synthesis of piperazine based macrocyclic phanes[6] and its application aspects such as photoresponsive properties[7] and inclusion complexes with acetonitrile were studied by Rissanen et al.[8] Though benzotriazole has been used for the synthesis of *N*-pivot lariat crown ethers,[9] its incorporation in a cyclophane ring system remains unexplored. Benzotriazolophanes might have increased complexing, chelating and solubilizing ability due to the presence of the greater number of heteroatoms and hence would be more promising than the imidazolophanes reported earlier from our laboratory.[5] We describe herein a simple route for the synthesis of benzotriazolophanes **2**, **3**, **4** and **5** of which **4** and **5** have *m*-terphenyl building block. The dicationic benzotriazolophanes **2**, **3** and **4** could be a potential precursor for the synthesis of [2]-catenanes. Moreover the cross-linked benzotriazolophane **5** could be the precursor for the synthesis of [3]-catenanes.



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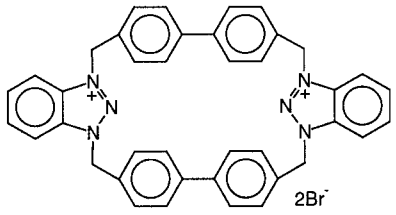

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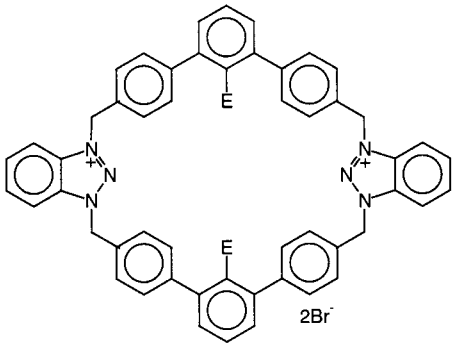

E = H, Br, COOH, COOMe

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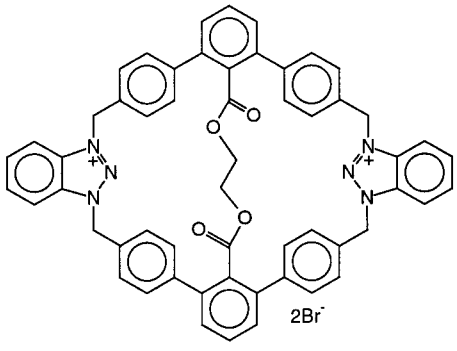

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Keywords: benzotriazoles; alkylation; cyclization.
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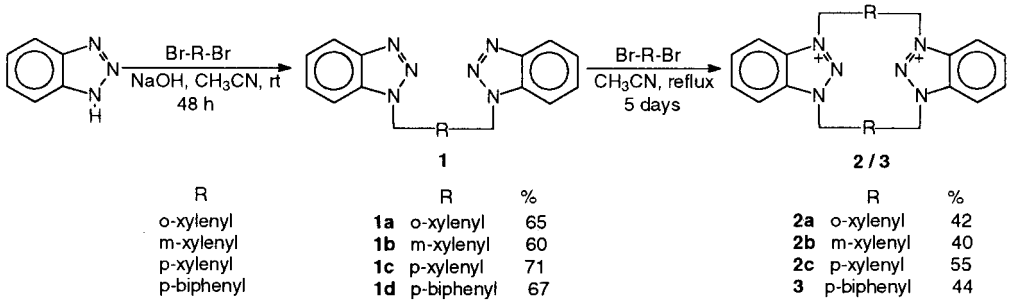


Scheme 1.

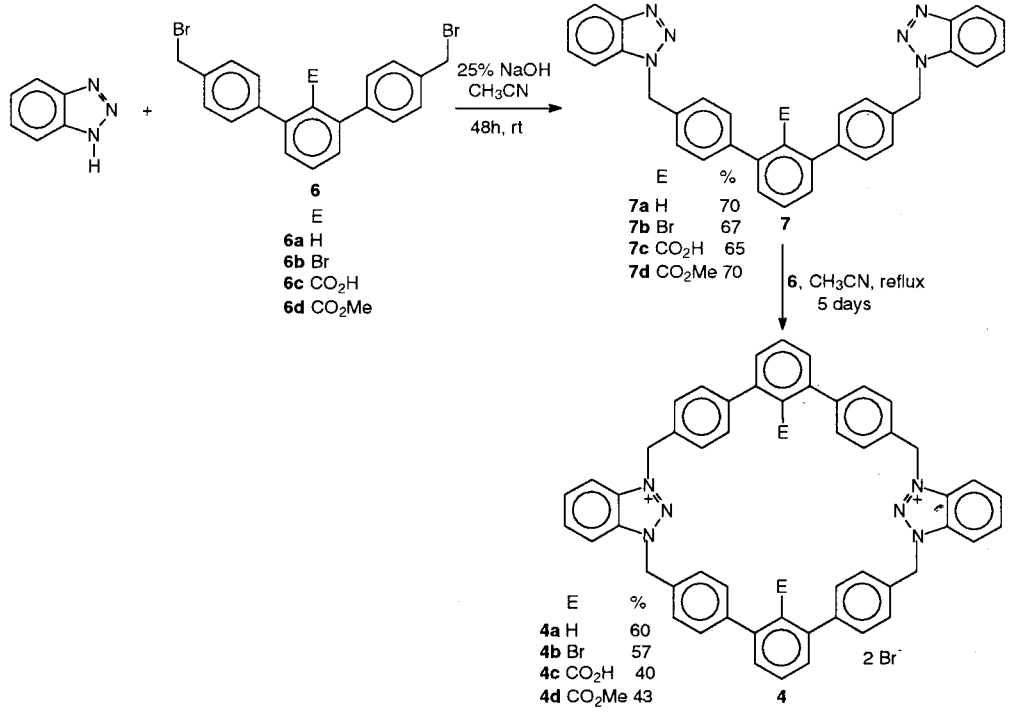
Results and Discussion

In order to test the utility of benzotriazole for the synthesis of cyclophanes, two equivalents of benzotriazole was reacted with one equivalent of *o*-xylenyl dibromide in CH_3CN in the presence of NaOH. The reaction mixture after workup afforded the *N*-alkylated product **1a** (65%, mp 172°C). ^{1}H NMR of **1a** displayed a singlet for N–CH_2 at δ 5.79 in addition to the aromatic protons. Refluxing **1a** with one more equivalent of *o*-xylenyl dibromide for 5 days in CH_3CN gave the cyclophane **2a** in 42% yield. ^{1}H NMR of **2a** showed a singlet for N–CH_2 at δ 6.38 in addition to the aromatic protons. It is noteworthy to mention that quaternization occurs only at N-3 of benzotriazole.[10] Katritzky et al.[10] have reported that the yields of such quaternization vary from 66 to as low as 9% also depending upon the type of alkylating agent. Moreover after quaternization the benzotriazole protons in ^{1}H NMR resonate at δ 7.24–7.92 and 8.13–8.32.[11] This observation clearly supports the fact that quaternization in benzotriazole occurs at N-3 rather than at the N-2 position. A similar synthetic strategy was adopted for the synthesis of benzotriazolophanes **2b**, **2c** and **3** as outlined in Scheme 1.

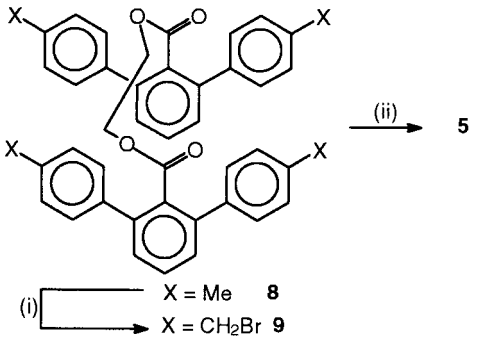
In order to increase the cavity size in benzotriazolophanes, *m*-terphenyl dibromide and their derivatives were used. The *m*-terphenyl frame work in **4** and **5** is obtained by the known tandem aryne sequence.[12] *m*-Terphenyl derivatives **6**, **6a**, **6b** and **6c** were prepared from 2,6-dichloroiodobenzene as reported earlier.[13] Similarly the tetrabromide **9** was prepared from the ethylene glycol ester **8**.[14]

Reaction of 2.1 equiv. of benzotriazole with 1 equiv. of *m*-terphenyl dibromide **6a** gave the monoalkylated product **7a** as a colorless solid, which on further reaction with one more equivalent of **6a** gave the cyclophane **4a** as a colorless solid. ^{1}H NMR of **4a** showed a singlet at δ 6.40 for N–CH_2 in addition to the aromatic protons. Similarly triazolophanes **4b**, **4c** and **4d** were prepared from the monoalkylated derivatives **7b**, **7c** and **7d**, respectively as shown in Scheme 2.

Two fold coupling of the tetrabromide **9** with 2.1 equiv. of benzotriazole afforded the benzotriazolophane **5** in 40% yield. ^{1}H NMR of **5** showed singlets at δ 3.50 for four protons (O–CH_2) and at δ 5.93 for eight protons (N–CH_2) (Scheme 3).



Scheme 2.



Scheme 3.

Cross-linking with various alkyl bromides after reducing the cyclophane **4** and the ability of these cyclophanes to chelate with metal ions are under investigation.

Conclusion

Novel and unprecedented benzotriazolophanes **2**, **3**, **4** and **5** were prepared in moderate yield in two steps by alkylation followed by quartinization of benzotriazole with various dibromides or tetrabromide. As the cyclophanes reported herein are positively charged they could be expected to trap anions and guest molecules with high electron density. Reduction of 1,3-dialkylbenzotriazolium salt with NaH results in the formation of 1,3-dialkyl[2*H*]benzotriazole. From this model reaction, reduction of benzotriazolophanes with NaH in THF could result in the formation of [2*H*]-benzotriazolophanes which could be further intramolecularly alkylated to give cross-linked cyclophanes.

Experimental

^{1}H NMR and ^{13}C NMR were obtained on Jeol 400 MHz instrument with $CDCl_3$ and DMSO-d_6 as the solvents. Chemical shifts are expressed in ppm using TMS as internal standard. Coupling constant (*J*) values are given in Hz. IR spectra were recorded on a FTIR-8300 Shimadzu machine. Mass spectra were recorded on Finnigan MAT 8430 by EI (NH_3) and FAB (Matrix-NBA). Dry acetonitrile was freshly prepared prior to use. The precyclophanes were purified by using neutral alumina column with $CHCl_3$:hexane (7:3) as solvent, with a flow rate of 1 mL/min.

General procedure for the synthesis of precyclophanes (1 and 7)

To the solution of benzotriazole (20 mmol) in acetonitrile (50 mL), NaOH solution (7.5 mL, 25%) was added and stirred for 10 min. The dibromide (10 mmol) in acetonitrile (10 mL) was added at once and stirred for two days at room temperature. After the completion of the reaction, the reaction mixture was evaporated in vacuo and extracted with $CHCl_3$ (4×50 mL), washed with saturated NaCl (2×50 mL) and dried ($MgSO_4$) and the solvent evaporated in vacuo. The crude product was purified by column chromatography.

Precyclophane 1a. White solid, mp 172°C; [Found: C, 70.45; H, 4.62; N, 24.56. $C_{20}H_{16}N_6$ requires C, 70.59; H, 4.71; N, 24.70%]; ν_{max} (KBr) 3060, 2914, 2362, 2332, 1679, 1614, 1448, 1311, 1151 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.79 (4H, s, N–CH_2), 7.19–7.39 (10H, m, ArH), 8.06 (2H, d, *J*=8.0 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 51.9, 109.5, 120.2, 124.0, 126.7, 127.6, 127.7, 129.9, 132.7, 135.8, 146.3; *m/z* (EI, NH_3) 340 (M^+).

Precyclophane 1b. White solid, mp 181°C; ν_{max} (KBr) 3030, 2925, 2362, 2335, 1679, 1614, 1487, 1448, 1311, 1151, 1118 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.01 (4H, d, *J*= 6 Hz, N–CH_2), 7.14–7.44 (10H, m, ArH), 8.08 (2H, d, *J*= 8 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 49.7, 109.6, 120.2, 124.2, 127.9, 129.3, 133.0, 133.2, 146.2; *m/z* (EI, NH_3) 340 (M^+).

Precyclophane 1c. White solid, mp 120°C; ν_{max} (KBr) 3054, 2912, 1360, 2331, 1672, 1615, 1442, 1302, 1156 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.83 (4H, s, N–CH_2), 7.34 (6H, m, ArH), 7.37 (4H, s, ArH), 8.04 (2H, d, *J*= 10.0 Hz, ArH), δ_C (100.6 MHz, $CDCl_3$) 51.7, 59.8, 109.6, 118.1, 120.1, 124.0, 126.5, 127.5, 128.1, 128.0, 130.4, 132.7, 135.0, 135.3, 144.6, 146.3; *m/z* (EI, $NH_{3)}$ 340 (M^+).

Precyclophane 1d. White solid, mp 162°C; [Found: C, 74.89; H, 4.78; N, 20.09. $C_{26}H_{20}N_6$ requires C, 75.00; H, 4.81; N, 20.19%]; ν_{max} (KBr) 3032, 2913, 2360, 2339, 1684, 1612, 1439, 1317, 1147 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.82 (4H, d, *J*=6.0, N–CH_2), 7.12–7.92 (14H, m, ArH), 8.23 (2H, d, *J*=8.0 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 51.9, 60.0, 109.6, 118.1, 120.1, 123.9, 126.4, 127.4, 127.5, 127.6, 128.0, 134.0, 140.6, 144.6; *m/z* (EI, $NH_{3)}$ 416(M^+).

Precyclophane 7a. White solid, mp 176°C; [Found: C, 77.95; H, 4.79; N, 16.99. $C_{32}H_{24}N_6$ requires C, 78.05; H, 4.88; N, 17.07%]; ν_{max} (KBr) 3012, 2924, 2363, 2345, 1681, 1623, 1432, 1312, 1154 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.87 (4H, s, N–CH_2), 7.40 (2H, d, *J*=7.8 Hz, ArH), 7.45 (8H, ABq, *J*=8.0 Hz, ArH), 7.48 (7H, m, ArH), 7.67 (1H, s, ArH), 8.07 (2H, d, *J*=8.0 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 51.8, 109.6, 120.0, 123.9, 125.8, 126.2, 127.4, 127.7, 128.0, 129.2, 132.7, 133.9, 140.8, 141.1, 146.3; *m/z* (EI, NH_3) 492(M^+).

Precyclophane 7b. White solid, mp 148°C; ν_{max} (KBr) 3018, 2918, 2358, 2338, 1679, 1632, 1418, 1319, 1151 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.88 (4H, s, N–CH_2), 7.21 (2H, d, *J*=7.7 Hz, ArH), 7.35 (8H, ABq, *J*=8.0 Hz, ArH), 7.44 (7H, m, ArH), 8.07 (2H, d, *J*=8.0 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 51.9, 109.7, 120.1, 124.0, 125.5, 127.1, 127.2, 128.2, 130.1, 130.3, 132.9, 134.0, 142.0, 143.0, 146.3; *m/z* (EI, NH_3) 570(M^+).

Precyclophane 7c. White solid, mp 176°C; [Found: C, 73.55; H, 4.40; N, 15.50. $C_{33}H_{24}N_6O_2$ requires C, 73.88; H, 4.48; N, 15.67%]; ν_{max} (KBr) 3012, 2924, 2363, 2345, 1696, 1623, 1432, 1312, 1154 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.89 (4H, s, N–CH_2), 7.23 (2H, d, *J*=8.0 Hz, ArH), 7.39 (8H, ABq, *J*=8.0 Hz, ArH), 7.42 (7H, m, ArH), 8.00 (2H, d,

J=8.0 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 52.3, 110.6, 119.6, 123.3, 124.9, 126.3, 127.4, 127.6, 128.2, 129.3, 133.3, 133.7, 137.7, 142.6, 146.3, 172.2; m/z (EI, NH_3) 536(M^+).

Precyclophane 7d. White solid, mp 176°C; ν_{max} (KBr) 3012, 2924, 2363, 2345, 1723, 1681, 1623, 1432, 1312, 1154 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.25 (3H, s, OCH_3), 5.86 (4H, s, N–CH_2), 7.29 (9H, m, ArH), 7.35 (8H, ABq, J=8.8 Hz, ArH), 8.06 (2H, d, J=8.0 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 31.5, 51.9, 109.7, 118.1, 120.1, 124.0, 126.5, 127.6, 128.2, 129.0, 129.7, 132.6, 132.0, 140.6, 144.6, 146.3, 169.5; m/z (EI, NH_3) 550(M^+).

General procedure for the synthesis of cyclophanes (2, 3 and 4)

To the solution of precyclophane (6 mmol) in dry acetonitrile (400 mL), dibromide (6 mmol) was added at once and refluxed for five days. After completion of the reaction the cyclophane was obtained by filtration of the reaction mixture. The cyclophane was thoroughly washed with acetonitrile and dried in vacuo.

Cyclophane 2a. White solid, mp 178°C; [Found: C, 63.87; H, 4.12; N, 15.76. $C_{28}H_{24}Br_2N_6$ requires C, 64.12; H, 4.58; N, 16.03%]; ν_{max} (KBr) 3012, 2943, 2358, 1612, 1534, 1439, 1369, 1268, 1133, 1016 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.38 (8H, s, N–CH_2), 7.37 (8H, m, ArH), 7.74 (4H, dd, J=6.8, 3.0 Hz, ArH), 8.22 (4H, dd, J=6.8, 3.0 Hz, ArH); δ_C (100.6 MHz, DMSO-d_6) 53.4, 113.8, 129.9, 130.9, 131.3, 131.6, 133.7, 133.9, 135.4; m/z (EI, NH_3) 524(M^+-Br), 444(M^+-2Br).

Cyclophane 2b. White solid, mp 184°C; [Found: C, 63.87; H, 4.16; N, 15.84. $C_{28}H_{24}Br_2N_6$ requires C, 64.12; H, 4.58; N, 16.03%]; ν_{max} (KBr) 3023, 2956, 2349, 1632, 1529, 1449, 1329, 1264, 1054 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.43 (8H, s, N–CH_2), 7.30 (8H, m, ArH), 8.59 (4H, dd, J=7.0, 3.0 Hz, ArH), 8.03 (4H, dd, J=7.0, 3.0 Hz); δ_C (100.6 MHz, DMSO-d_6) 50.6, 110.5, 119.5, 124.4, 124.6, 125.5, 127.5, 128.3, 129.5, 130.1; m/z (EI, NH_3) 524(M^+-Br), 444(M^+-2Br).

Cyclophane 2c. White solid, mp 233°C; [Found: C, 63.89; H, 4.21; N, 15.69. $C_{22}H_{24}Br_2N_6$ requires C, 64.12; H, 4.58; N, 16.03%]; ν_{max} (KBr) 3018, 2934, 2354, 1632, 1545, 1429, 1353, 1263, 1143, 1029 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.26 (8H, s, N–CH_2), 7.28 (2H, s, ArH), 7.56 (2H, bs, ArH), 7.86 (4H, bs, ArH), 7.96 (4H, bs, ArH), 8.49 (4H, bs, ArH); δ_C (100.6 MHz, DMSO-d_6) 54.3, 114.5, 129.5, 130.1, 131.0, 132.0, 133.9, 135.0; m/z (EI, NH_3) 524 (M^+-Br), 444 (M^+-2Br).

Cyclophane 3. White solid, mp 212°C; [Found: C, 63.39; H, 4.18; N, 10.87. $C_{40}H_{32}Br_2N_6$ requires C, 63.49; H, 4.23; N, 11.11%]; ν_{max} (KBr) 3023, 2938, 2353, 1628, 1549, 1439, 1357, 1253, 1128, 1028 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.52 (8H, s, N–CH_2), 7.12–7.82 (20H, m, ArH), 7.96 (4H, bs, ArH); m/z (FAB, NBA) 676 (M^+-Br), 596 (M^+-2Br).

Cyclophane 4a. White solid, mp 230°C; [Found: C, 68.56; H, 4.14; N, 9.15. $C_{52}H_{40}Br_2N_6$ requires C, 68.72; H, 4.41; N, 9.25%]; ν_{max} (KBr) 3018, 2922, 2364, 2335, 1602, 1556, 1514, 1440, 1367, 1336, 1197, 1161, 1018 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.40 (8H, s, N–CH_2), 7.58–7.85 (24H, m, ArH), 8.00 (4H, bs, ArH), 8.51 (4H, bs, ArH); δ_C (100.6 MHz, DMSO-d_6) 54.4, 114.3, 126.4, 127.7, 129.2, 129.6, 131.6, 132.0, 134.8, 140.6; m/z (FAB, NBA) 828 (M^+-Br), 748 (M^+-2Br).

Cyclophane 4b. White solid, mp 221°C; [Found: C, 58.44; H, 3.53; N, 7.57. $C_{52}H_{38}Br_4N_6$ requires C, 58.54; H, 3.56; N, 7.88%]; ν_{max} (KBr) 3014 2927, 2360, 1606, 1510, 1448, 1371, 1325, 1272, 1197, 1153, 1016 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.45 (8H, s, N–CH_2), 7.04–7.78 (22H, m, ArH), 8.09 (4H, dd, J=6.8, 3.0 Hz, ArH), 8.53 (4H, dd, J=6.8, 3.0 Hz, ArH); δ_C (100.6 MHz, DMSO-d_6) 54.1, 114.2, 121.7, 127.6, 128.4, 130.4, 131.4, 132.4, 134.7, 140.8, 142.3; m/z (FAB, NBA) 986 (M^+-Br), 906 (M^+-2Br).

Cyclophane 4c. White solid, mp 217°C; [Found: C, 64.96; H, 3.89; N, 8.38. $C_{54}H_{40}Br_2N_6O_4$ requires C, 65.06; H, 4.02; N, 8.43%]; ν_{max} (KBr) 3023, 2917, 2359, 2328, 1698, 1612, 1559, 1523, 1436, 1352, 1312, 1178, 1152, 1023 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 6.44 (8H, s, N–CH_2), 7.23–7.56 (23H, m, ArH), 8.01 (4H, dd, J=9.0, 3.0 Hz, ArH), 8.55 (4H, dd, J=9.0, 3.0 Hz, ArH), 10.08 (1H, s, COOH); δ_C (100.6 MHz, DMSO-d_6) 54.3, 114.4, 119.3, 126.7, 128.3, 129.3, 132.2, 134.9, 138.1, 141.0, 145.4, 170.0; m/z (FAB, NBA) 916 (M^+-Br), 836 (M^+-2Br).

Cyclophane 4d. White solid, mp 207°C; [Found: C, 65.54; H, 4.23; N, 8.12. $C_{56}H_{44}Br_2N_6O_4$ requires C, 65.63; H, 4.30; N, 8.20%]; ν_{max} (KBr) 3012, 2923, 2368, 2339, 1724, 1572, 1447, 1269, 1105 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 3.28 (3H, s, OCH_3), 6.44 (8H, s, N–CH_2), 7.24–7.67 (25H, m, ArH), 8.04 (4H, bs, ArH), 8.49 (4H, bs, ArH); δ_C (100.6 MHz, DMSO-d_6) 52.1, 54.5, 114.5, 126.9, 128.7, 129.5, 130.5, 131.8, 132.3, 135.0, 139.1, 140.8, 169.2; m/z (FAB, NBA) 944 (M^+-Br), 864 (M^+-2Br).

Procedure for the synthesis of cross-linked cyclophane 5

To the solution of benzotriazole (0.08 mmol) in acetonitrile (50 mL), NaOH solution (1.5 mL, 25%) was added and stirred for 10 min. The tetrabromide (0.16 mmol) in acetonitrile (5 mL) was added at once and stirred for two days at room temperature. The reaction mixture was refluxed for another five days. After completion of the reaction, the cyclophane **5** was obtained by filtration of reaction mixture. The cyclophane was washed thoroughly with acetonitrile and dried in vacuo.

Cyclophane 5. White solid, (40%, 0.065 g), mp 246°C; [Found: C, 64.81; H, 3.79. $C_{56}H_{42}Br_2N_6O_4$ requires C, 65.63; H, 4.11%]; ν_{max} (KBr) 3022, 2915, 2362, 2344, 1728, 1587, 1458, 1239, 1138 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 3.50 (4H, s, OCH_2), 5.93 (8H, s, N–CH_2), 7.26–7.86 (26H, m, ArH), 8.05 (4H, bs, ArH); δ_C (100.6 MHz, DMSO-d_6) 51.7 (OCH_2), 61.9 (N–CH_2), 118.1, 126.5, 127.5, 129.0, 129.1, 129.7, 131.9, 132.6, 134.55, 138.7, 146.1, 173.3 (carbonyl); m/z (FAB, NBA) 942(M^+-Br), 862(M^+-2Br).

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