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Synthesis, molecular structure and optical spectral studies of *syn*-dithia benzothiazolophane and *anti*-bis-lactone benzothiazolophane

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Abstract

Synthesis of *syn*-dithia-benzothiazolophane **1** and *anti*-bis-lactone benzothiazolophane **2** has been carried out by well established protocols as outlined in Schemes 1 and 2, respectively. The ^{1}H NMR spectra of heterophanes **1** and **2** were found to be temperature independent in the range of -55 to $+120$ °C which indicates conformationally mobile nature of these molecules. In comparison to plain $CHCl_3$, the UV–visible spectra of **1** and **2** measured in $CHCl_3$ containing trifluoroacetic acid (TFAA) exhibited bathochromic shifts by 25 and 19 nm, respectively. The red shifts are attributed to the increased charge transfer interaction arising from the donor phenyl ring to the acceptor benzothiazolium ring. The emission spectra of thia-bridged **1**, both in the neutral as well as the protonated forms are accompanied by large Stokes shifts ($\Delta\nu = 127-156$ nm) with the emissions most likely originating from the locally excited states. The bis-lactone **2** in neutral $CHCl_3$ solvent also exhibited a single locally excited emission, but with a relatively lower Stokes shift ($\Delta\nu = 69$ nm). Interestingly, unlike **1**, bis-lactone **2** in the protonated form displayed both local as well as what appears to be an intramolecular charge transfer emission. The emission behavior of **1** and **2** has been tentatively rationalized on the basis of HOMO–LUMO interaction. Molecular modelling of **1** and **2** generated five reasonable conformations within 5 kcal/mol depending upon the orientation of the benzothiazole rings and the heteroatoms in the connecting bridges. The transannular distances in **1** and **2** were found to be ca. 2.8 and 3.6 Å, respectively. While the rings in **2** are nearly planar, however, in the case of **1** the stacks are slightly curved signifying molecular strain in the letter system. Based on dynamic ^{1}H NMR spectral analysis and molecular modelling, we propose that these molecules exist as a rapidly equilibrating mixtures of conformers.

Keywords: Benzothiazolophanes; Synthesis; Dynamic NMR; UV–visible; Fluorescence spectra; Local/charge transfer emissions

1. Introduction

Short bridged cyclophanes have been extensively used as molecular probes to study their conformational behavior and the effects of ring proximity on physical, spectral and chemical properties [1]. Numerous reports by Haenel, Misumi, Staab and others [2] concerning the ground and excited state properties of fluorescent active cyclophanes have clearly established the dependency of photophysical properties upon ring distortion, orientation and intrachromophoric distance between π-stacked fluorophores. Although, cyclophanes of polycyclic aromatics, viz naphthalene, anthracene, pyrene, fluorene abound [3–8], only a few examples of cyclophanes composed of heteroaromatic fluorophores, namely carbazolophanes have been described in Ref. [9]. 2-Aryl benzothiazoles, which find applications as whitening agents [10], photoconducting materials [11] and constituents of biologically active molecules [12] have been investigated for their solvatochromic and emission properties [13]. Indeed, Tashiro et al. [14] have recently described the synthesis and spectral properties of metacyclophanes containing benzothiazole as a peripheral substituent located outside the *phane* ring. In continuation of our interest in the synthesis and conformational properties of heterophanes [15], we herein describe for the first time the incorporation of arylbenzothiazole fluorophore as a constituent of the *phane* cavity in the form of heterophanes **1** and **2**. The synthesis of heterophanes **1** and **2** were of interest to us to study their absorption and emission characteristics with respect to differently oriented π-stacked benzothiazole chromophores. In addition, conformational behavior of **1** and **2** was of

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interest, since potential exists in these heterophanes to adopt a variety of conformations subject to conformational rigidity and depending up on the orientations of benzothiazole nuclei and the bridging heteroatoms.

2. Experimental

The melting points (uncorrected) were determined on a Gallenkamp melting-point apparatus. IR spectral data were recorded on a Shimadzu FTIR -4200 Spectrophotometer as a KBr disk. Fluorescence spectra were recorded on a Shimadzu spectrofluorometer RF-5301 PC. ^{1}H NMR spectra were recorded on Varian EM-360-L, 60 and 300 MHz spectrometers with tetramethylsilane as the internal standard. Mass spectra were recorded on GCMS-QP 5050A Shimadzu spectrophotometer.

2.1. Preparation of p-methoxymethylbenzothioamide *4*

p-methoxymethylbenzonitrile [16] (15 g, 102 mmol) was dissolved in a solution consisting of dry pyridine (30 ml) and triethylamine (3 ml) to which dry H_2S was bubbled through for 12 h. The reaction mixture was diluted with cold water, precipitated solid filtered and washed once with 10% HCl followed by cold-water washing. The air-dried solid was crystallized from ethanol to give **4** as yellow crystal, m.p. 113–116 °C in 76% yield (14 gm). IR (KBr): 3315, 3112, 3008, 1610, 1445, 1332, 1245, 1107, 964, 902, 827 cm^{-1} NMR (CDCl3, 60 MHz): δ 3.4 (3H, s, Ar CH_2OCH_3), 4.40 (2H, s, Ar CH_2OCH_3), 7.25 (2H, d, $J = 7$ Hz, Ar–H), 7.85 (2H, d, $J = 7$ Hz, Ar–H), 11.20 (2H,bs, $-NH_2$); Found: C, 59.43; H, 5.89; N, 7.68; S, 17.85. Calcd for $C_9H_{11}NOS$: C, 59.66; H, 6.07; N, 7.73; S, 17.68.

2.2. Preparation of methoxy-acid *5*

To a solution of 4-amino-3-mercapto-benzoic acid **3** [17] (5.50 g, 32.5 mmol) and 4-methoxymethyl benzothioamide **4** (4.525 g, 25 mmol) in dry *N*-methylpyrrolidone (50 ml) was added conc. HCl (5 ml) and the reaction was heated on water bath for 8 h. After allowing the reaction to cool to room temperature, it was poured over crushed ice. The precipitated solid was filtered, air-dried and crystallized from alcohol to give **5**, m.p. 260–265 °C in 80% yield (6 g); IR (KBr): 3414, 3000, 2988, 1720, 1600, 1482, 1414, 1300, 1245, 1200, 1005, 966 and 844 cm$^{-1;}$ ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.53 (s, 2H, PhCH_2OCH_3), 3.46 (s, 3H, PhCH$_2$OCH_3), 7.46–8.64 (m, 7H, Ar–H), 11.5 (bs, 1H, –COO*H*; Found: C, 64.39; H, 4.18; N, 4.87; S, 10.65%. Calcd for $C_{16}H_{13}NO_3S$: C, 64. 21; H, 4.35; N, 4.68; S, 10.70%.

2.3. Preparation of bromo-acid *6*

Methoxy-acid **5** (7 g, 23.4 mmol) was dissolved in 39% aqueous HBr (100 ml) and heated on water bath for 10 h. The reaction was diluted with water and refrigerated overnight. The precipitated solid was filtered, washed with cold water and finally dried in air to give essentially pure **6**, m.p. 350 °C decomp. in 86% yield (7.05 g); IR (KBr): 3420, 3010, 2928, 1700, 1605, 1565, 1480, 1415, 1330, 1300, 1245, 1122, 1005, 940 and 835 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.78 (s, 2H, PhCH_2Br), 7.40–8.80 (m, 7H, Ar–H), 13.2 (bs, 1H, –COO*H*); IR; Found: C, 51.49; H, 2.66; N, 4.23; S, 9.32; Br, 23.17%. Calcd for $C_{15}H_{10}NSO_2Br$: C, 51.72; H, 2.87; N, 4.02; S, 9.19; Br, 22.99%.

2.4. Preparation of bromo- ester *7*

Bromo-acid **6** (7.0 g, 20.12 mmol) was dissolved in dry methanol (100 ml) and $SOCl_2$ (15 ml) was added drop-wise at 0–5 °C during 15 min. The reaction was allowed to come to room temperature and then heated to reflux for 24 h. The solvent was removed under reduced pressure and the residual oil dissolved in chloroform, washed successively with a saturated aqueous $NaHCO_3$ and cold water. The organic extract was dried over anhyd. Na_2SO_4 and solvent removed to give a crude solid. Purification was effected by SiO_2 column chromatography ($CHCl_3$ as eluent) to furnish **7** as white solid in 48% yield (3.5 g), m.p. 150–155 °C; IR (KBr disk): 3015, 2914, 1710, 1619, 1595, 1460, 1435, 1380, 1310, 1225, 1162, 1000, 980 and 815 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.62 (s, 2H, PhCH_2Br), 3.98 (s, 3H, –COOCH_3), 7.40–8.72 (m, 7H, Ar–H); Found: C, 52.87, H, 3.47; N, 4.03; S, 8.93; Br, 22.33%. Calcd for $C_{16}H_{12}NSO_2$-Br: C, 53.04; H, 3.31; N, 3.87; S, 8.84; Br, 22.09%.

2.5. Preparation of thia-diester *8*

To a solution of bromo-ester **7** (2.65 g, 7.32 mmol) in 100 ml dry CH_2Cl_2 was added a catalytic amount of CTAB (50 mg), followed by portion-wise addition of anhyd. Na_2S (1.5 g, 19.23 mmol) during 8 h with vigorous stirring. The reaction was stirred further at room temperature for 48 h and then filtered through a pad of celite. The filtrate was concentrated to give a semi-solid residue which was purified by SiO_2 column chromatography ($CHCl_3$ as eluent) to furnish **8** as a pale-yellow crystalline solid in 89% yield (1.95 gm), m.p. 180–185 °C.; IR (KBr): 3025, 2910, 1712, 1600, 1485, 1424, 1415, 1295, 1240, 1110, 960, 845 and 780 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.7 (s, 4H, PhCH_2S–), 4.0 (s, 6H, –COOCH_3), 7.40–8.6 (m, 14H, Ar–H); Found: C, 64.68; H, 4.29; N, 4.31; S, 16.35%. Calcd for $C_{32}H_{24}N_2O_4S_3$: C, 64.43; H, 4.03; N, 4.69; S, 16.11%.

2.6. Preparation of diol *9*

The solid diester **8** (1.4 g, 2.35 mmol) was added portion-wise to a slurry of $LiAlH_4$ (500 mg, 15 mmol) in dry THF (100 ml) under N_2 atmosphere during 1 h. The reaction mixture was stirred an additional 1 h and decomposed at 0 °C by careful addition of 3 ml of 15% NaOH and 10 ml

H_2O. The reaction mixture was stirred for 15 min, filtered through celite and the filtrate concentrated under reduced pressure to give an oily residue. Purification by SiO_2 column chromatography using $CHCl_3$ as eluent provided **9** in 45% yield (0.570 g), m.p. 185–190 °C; IR (KBr): 3005, 2950, 1610, 1495 and 980 cm^{-1}; H^1 NMR (300 MHz, $CDCl_3$): δ 4.72 (s, 4H, Ph*CH*$_2$OH), 3.62 (s, 4H, Ph*CH*$_2$S–), 7.20–8.1 (m, 14H, Ar–H); Found: C, 66.35; H, 4.63; N, 5.32; S, 17.54%. Calcd for $C_{30}H_{24}N_2O_2S_3$ requires: C, 66.66; H, 4.44; N, 5.19; S, 17.77%.

2.7. Preparation of thia-dibromide *10*

Diol **9** (900 mg, 1.66 mmol) was stirred with 33% HBr in acetic acid (40 ml) for 4 h at room temperature. The reaction was diluted with cold water and extracted with chloroform. The organic extract was washed well with cold saturated $NaHCO_3$ solution and then with cold water. The organic extract after drying over anyd. Na_2SO_4 was concentrated under reduced pressure to afford a yellow solid, which was further purified by SiO_2 column chromatography ($CHCl_3$–petroleum ether 1:1 as eluent) to give **10** in 77% yield (850 mg), m.p. 195–200 °C; IR (KBr): 3000, 2940, 1610, 1480, 1455, 1315, 974 and 822 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.65 (s, 4H, Ph*CH*$_2$Br), 3.70 (s, 4H, Ph*CH*$_2$S–), 7.20–8.20 (m, 14H, Ar–H); Found: **C**, 54.38; H, 3.19; N, 3.98; S, 14.16; Br, 24.36%. Calcd for $C_{30}H_{22}N_2S_3Br_2$: C, 54.05; H, 3.30; N, 4.20; S; 14.41; Br, 24.02%.

2.8. Preparation of syn-dithia-phenylbenzothiazolophane *1*

A solution of dibromide **10** (500 mg, 0.751mmol) in dry THF (100 ml) was added drop-wise to a stirred solution of dry THF-benzene (1:1, 200 ml) containing anhyd. Na_2S (500 mg, 6.4 mmol) and CTAB (20 mg) during 10 h under N_2 atmosphere. The reaction mixture was further stirred at room temperature for 72 h and filtered through a pad of celite. The filtrate was concentrated to provide a yellow solid which was purified by SiO_2 column chromatography ($CHCl_3$–petroleum ether, 3:1 as eluent) to give **1** as a pale-yellow solid in 37% yield (150 mg), m.p. 270–275 °C; IR (KBr): 3012, 2914, 1610, 1485, 1465, 1410, 1305, 1208, 1106, 964, 842, 802 and 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 4H, Ph*CH*$_2$S), 3.82 (s, 4H, Bz*CH*$_2$S–), 6.8 (d, 1H, $J = 1.5$ Hz, H7 of Bz), 6.95 (d, 2H, $J = 7.5$ Hz, ArH), 7.30 (d, 1H, $J = 7$ Hz, H4 of Bz), 7.45 (d, 2H, $J = 7.5$ Hz, ArH), 7.72 (dd, 1H, $J = 7.0$ and 1.5 Hz, H5 of Bz); Found: C, 66.75; H, 4.35; N, 5.05; S, 23.62%. Calcd for $C_{30}H_{22}N_2S_4$ requires: C, 66.91; H, 4.09; N, 5.20; S, 23.79%; MS: *m/z* 538 (M^+), 268, 238 (base peak), 121, 77.

2.9. Preparation of methoxy-acid *12*

4-Amino-3-mercapto-benzeneacetic acid **11** [18] (1.83 g, 10 mmol) and 4-methoxymethyl benzothioamide **4** (1.81 g, 10 mmol) were dissolved in *N*-methylpyrrolidone (25 ml) containing 1 ml of conc. HCl. The reaction was heated on water bath for 70 h, then diluted with cold water and left at room temperature overnight. The precipitated solid was filtered, washed with cold water and air-dried. The crude product was subjected to SiO_2 column chromatography ($CHCl_3$ as eluent) to give yellow crystals of **12**, m.p. 155–158 °C in 58% yield (1.8 g). IR (KBr): 3100, 2912, 1713, 1508, 1456, 1405, 1310, 1216, 1100, 986 and 807 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 3.8 (s, 2H, Ph*CH*$_2$COOH–), 3.45 (s, 3H, PhCH$_2$O*CH*$_3$), 4.55 (s, 2H, Ph*CH*$_2$OCH$_3$), 7.2–8.2 (m, 7H, Ar–H), 11.78 (bs, 1H, –COO*H*); Found: C, 64.95; H, 4.51; N, 4.12; S, 10.46%. Calcd for $C_{17}H_{15}NO_3S$: C, 65.18; H, 4.79; N, 4.41; S, 10.22%.

2.10. Preparation of bromo-acid *13*

Methoxy-acid **12** (2.05 g, 6.4 mmol) was dissolved in 50 ml of 37% aqueous HBr and heated on water bath for 10 h. The reaction mixture was diluted with cold water, the precipitated solid filtered, washed with cold water and finally dried in open air to afford essentially pure **13** in 80% (1.84 g), m.p. 215–218 °C; IR (KBr): 3406, 2912, 1712, 1586, 1500, 1405, 1376, 1310, 1212, 1000, 845 and 805 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 3.77 (s, 2H, Ph*CH*$_2$COOH), 4.78 (s, 3H, Ph*CH*$_2$Br), 7.4–8.2 (m, 7H, Ar–H), 12.8 (bs, 1H, –COO*H*); Found: C, 52.89; H, 3.25; N, 4.13; S, 9.02; Br, 22.35%. Calcd for $C_{16}H_{12}NO_2SBr$: C, 53.04; H, 3.31; N, 3.87; S, 8.84; Br, 22.09%.

2.11. Preparation of anti-bis-lactone benzothiazolophane *2*

A solution of bromo-acid **13** (1.452 g, 4 mmol) in dry THF was added drop-wise to a stirred THF (250 ml) containing anhyd. K_2CO_3 (1.38 g, 10 mmol) and CTAB (50 mg) during 10 h with vigorous stirring at 50–55 °C under N_2 atmosphere. The reaction was additionally stirred at this temperature for 24 h and then filtered through celite. After usual work up, a semi-solid residue obtained was subjected to SiO_2 column chromatography ($CHCl_3$–CH_3OH, 95:5 as eluent) to afford **2** as a white crystalline solid, m.p. >300 °C in 13% yield (0.150 g). IR (KBr disk): 3000, 2980, 1723, 1485, 1454, 1412, 1360, 1310, 1242, 1122, 1105, 986 and 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.2 (s, 4H, 4H, Ph*CH*$_2$OCO–), 3.70 (S, 4H, –OCO–*CH*$_2$–Ph), 7.05 (d, 2H, $J = 7.5$ Hz, ArH), 7.15 (d, 1H, $J = 1.5$ Hz, H7 of Bz), 7.42 (d, 1H, $J = 7$ Hz, H4 of Bz), 7.51 (d, 2H, $J = 7.5$ Hz, ArH), 7.92 (dd, 1H, $J = 7.0$ and 1.5 Hz, H5 of Bz); Found: C, 68.62; H, 3.75; N, 5.01; S, 11.48%. Calcd for $C_{32}H_{22}N_2O_4S_2$: C, 68.33; H, 3.91; N, 4.98; S, 11.39%; MS: *m/z* 562 (M^+), 474, 259, 237 (base peak), 121, 77, 44.

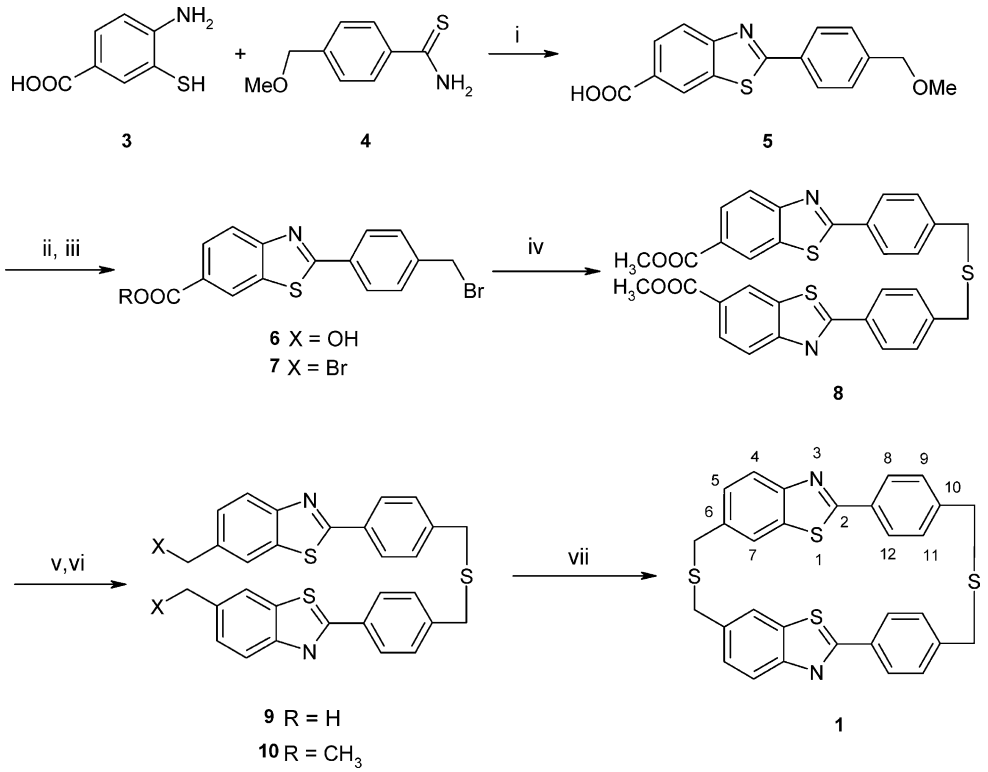
3. Results and discussion

The sequence used for the synthesis of *syn*-dithia [3.3] phenyl benzothiazolophane **1** is depicted in Scheme 1. To start with, the known 4-amino-3-mercapto-benzoic acid **3** [17] was condensed with 4-methoxymethyl benzothioamide **4** in *N*-methyl pyrrolidone (NMP) solvent containing ca. 2 equivalent of conc. HCl. The reaction provided benzothiazole derivative **5** in 80% yield. The demethylation of **5** was achieved with 49% aq. HBr under reflux to afford bromo-acid **6** as a colorless solid (86% yield). Esterification of **6** with $SOCl_2$ in dry methanol gave quantitatively the methyl ester **7**. Next, to form the mono-thia bridged **8**, bromo-ester **7** was reacted with Na_2S in methylene chloride solvent containing a catalytic amount of cetyl trimethylammonium bromide (CTAB) as the phase transfer catalyst. The diester **8** thus obtained was reduced to diol **9** with $LiAlH_4$ in dry THF. Treatment of **9** with 33% HBr–AcOH afforded dibromide **10** as colorless solid in good yield. The final step of the sequence, namely the formation of the second thia-bridge was effected under high dilution conditions by reacting **10** with Na_2S in 1:1 THF-benzene solvent containing a catalytic amount of CTAB. The work-up of the reaction, followed by purification of the crude by SiO_2 column chromatography afforded heterophane **1** in reasonable yield of 37%.

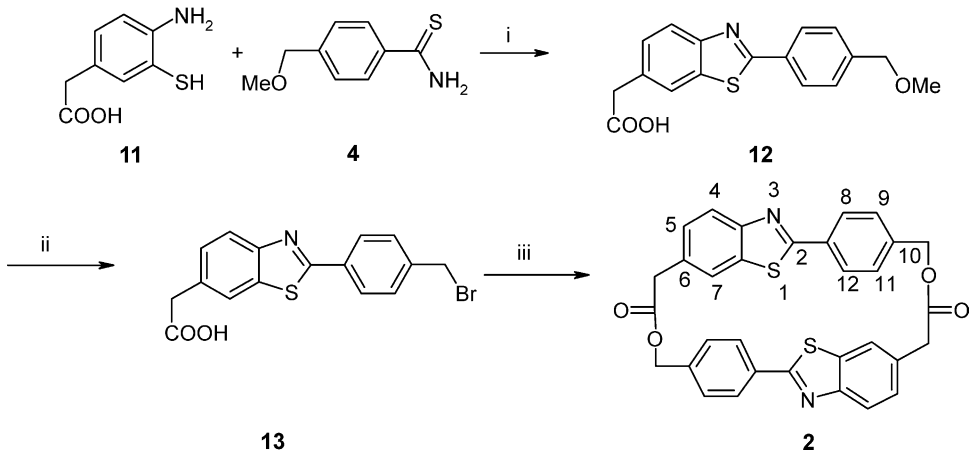
The synthesis of lactone bridged [4.4] *anti*-phenyl benzothiazolophane **2** (Scheme 2) starts with the condensation of known 4-amino-3-mercaptobenzene acetic acid (**11**) [18] with benzothioamide **4** in NMP under acid catalysis. The reaction gave the desired methoxy-acid **12** in 58% yield. The compound **12** was demethylated with 49% aq. HBr at 100 °C for 6 h to produce bromo-acid **13** in 80% yield. The final step in the sequence involved lactonisation of 13 which was accomplished under the Regen's protocol [19] in dry THF solvent in the presence of anhydrous K_2CO_3 and a catalytic amount of CTAB as the phase transfer catalyst. The purification of the crude product on SiO_2 column chromatography afforded the required bis-lactone **2** as a colorless solid in 13% yield.

3.1. Structures and conformational analysis of *1* and *2* by ^1H NMR spectroscopy

The structures of heterophanes **1** and **2** were characterized by ^1H NMR spectral data ($CDCl_3$, 500 MHz) which are compiled in Table 1. The dithia *syn*-**1** (M^+ at *m*/*z* 538) in its ^1H NMR spectrum showed singlets at 3.75 and 3.82 δ for the bridged $-CH_2-$ groups attached to the phenyl and benzothiazole moieties, respectively. The benzothiazole protons H4, H5 and H7 were observed at 7.30 (d, $J = 1.5$ Hz), 7.72 (dd, $J = 7$ and 1.5 Hz) and 6.85 δ (d, $J = 1.5$ Hz), respectively. As a consequence of shielding ring anisotropic effect, the H7 proton of the benzothiazole moiety is shifted higher field by 0.9 δ relative to the position of the corresponding proton in the reference compound, 2-phenylbenzothiazole (PBT) [20]. The phenyl protons appear as a doublet each ($J = 7.5$ Hz) at 7.45 and 6.95 δ,



Scheme 1. Synthesis of *syn*-dithia-**1** Reagents and conditions: (i) dry NMP, 70–90° C, 72 h. (ii) 33% aq. HBr, Δ, 8 h. (iii) $SOCl_2$, CH_3OH, reflux. 1 h (iv) Na_2S, CH_2Cl_2, CTAB, 24 h. (v) $LiAlH_4$, dry THF, 0 °C, 8 h. (vi) 33%HBr-AcOH, Δ, 8 h. (vii) Na_2S, dry THF-benzene, CTAB, R.T., 72 h.



Scheme 2. Synthesis of *anti*-bislactone-**2**. Reagents and conditions. (i) dry NMP, 70–90°C, 72 h. (ii) 33% aq. HBr, Δ, 8 h. (iii) K_2CO_3, dry THF, N_2, 60–65°C, 48 h.

respectively. For the case of bis-lactone **2**, the molecule (M^+ at *m*/*z* 562) exhibited two sharp singlets at 3.70 and 5.26 δ which are assigned to the bridged $-CH_2CO_2-$ and $-CH_2O-$ methylene groups, respectively. The benzothiazole ring protons H4, H5 and H7 appear at 7.92 (d, $J = 7.6$ Hz), 7.42 (dd, $J = 7.6$ and 1 Hz) and 7.15 δ (d, $J = 1$ Hz), respectively. The shielding being experienced by the H7 proton of the benzothiazole ring in **2** (0.60 δ with respect to PBT) is found to be lower than that observed in dithia *syn*-**1** (0.90 δ). In comparison to **1**, lower shielding of H7 proton in bis-lactone **2** is not unexpected on account of longer bridges (i.e. increased transannular distance) between the proximate aromatic rings. In keeping with this reduced degree of shielding, the phenyl protons in **2** appear slightly less upfield at 7.51 and 7.05 δ compared to the corresponding protons in **1** (7.45 and 6.95 δ).

The sharp singlets observed for the bridged methylene protons for both **1** and **2** clearly imply free bridge inversions in these molecules on the NMR time scale at ambient condition. The dynamic NMR measurements carried out from room temperature down to −55 °C indicated no signal broadening in the spectra of **1** and **2**, with the singlets associated with the bridged $-CH_2-$ retaining their singlet character. Thus, on the basis of unhindered bridge inversions occurring at least up to −55 °C in **1** and **2**, we can estimate the energy barrier for this process to be <40 kJ/mol [21]. Further, to check whether or not the rings are undergoing flipping, we measured NMR up to +120 °C. However, no changes either in the chemical shift position or multiplicities of aromatic protons were discernible. This result indicates one of the two possibilities; either the rings are undergoing free ring flippings giving rise to a time averaged conformation (i.e. fast interconversion between various conformers) or the molecules **1** and **2** exist as a single predominant, non-convertible conformer up to a temperature of 120 °C.

Since, benzothiazole ring contains a basic nitrogen, it was of interest to examine the ^{1}H NMR spectra of **1** and **2** in the presence of TFAA which is acidic enough to protonate the benzothiazole ring ($pK_a = 1.2$) [22]. In $CDCl_3$ containing TFAA, the molecules **1** and **2** were found to undergo bis-protonation as evidenced by the appearance of only a single set of resonance corresponding to half of the molecules (Table 1). In the case of **1** − $2H^+$, all the signals although slightly broad are reasonably well resolved and their assignments are based on the chemical shift positions and spin multiplicities. As expected, placing positive charge on the benzothiazole nuclei resulted in the downfield shifts of all the protons, the magnitude of shielding being dependent upon the positions of protons on the molecules. In **1** − $2H^+$ system, the benzylic protons at C6 and C10 are located slightly downfield at δ 4.03 and 3.94 compared to neutral **1** (Table 1) and the downfield shifts observed for benzothiazole ring protons range from δ 0.13 to 0.57, the highest

Table 1
^{1}H NMR data of **1** and **2** in $CDCl_3$ and $CDCl_3$ +TFAA

Proton type	**1**	**1** + $2H^+$	**2**	**2** + $2H^+$
C6($-CH_2$)	3.82 (s)	4.03 (s)	3.70 (s)	4.03 (s)
C10($-CH_2$)	3.75 (s)	3.94 (s)	5.20 (s)	5.30 (s)
H4	7.3 (d, $J = 7$ Hz)	7.66 (d, $J = 7$ Hz)	7.42 (d, $J = 7$ Hz)	7.74[a] (bs)
H5	7.72 (d, $J = 1.5$ Hz)	7.85 (d, $J = 1.5$ Hz)	7.92 (dd, $J = 7$ and 1.5 Hz)	8.08 (dd, $J = 7$ and 1.5 Hz)
H7	6.8 (dd, $J = 7$ and 1.5 Hz)	7.37	7.15 (d, $J = 1.5$ Hz)	7.44 (d, $J = 1.5$ Hz)
H8,12	7.4 (d, $J = 7.5$ Hz)	7.73 (d, $J = 7.5$ Hz)	7.51 (d, $J = 7.5$ Hz)	7.74[a] (bs)
H9,11	6.95 (d, $J = 7.5$ Hz)	7.37 (d, $J = 7.5$ Hz)	7.05 (d, $J = 7.5$ Hz)	7.27 (d, $J = 7.5$ Hz)

[a] Protons H4, H8, H12 showed identical chemical shifts.

downfield shift of δ 0.57 being noted for the C7 proton. The protons on the benzo-ring in $\mathbf{1} + 2H^+$ showed downfield shift in the range of δ 0.28–0.42 compared to the neutral **1**. Almost similar trend is noticeable for the bis-lactone **2**. However, protons located on C4 and C8, C12 could not be separately assigned due to accidentally identical chemical shift. The assignments for remaining protons are shown in Table 1. Interestingly, the downfield shifts observed for the benzothiazole protons in $\mathbf{2} - 2H^+$ are markedly lower (δ 0.23–0.32) compared to $\mathbf{1} - 2H^+$ (δ 0.28–0.42). This observation clearly suggests that the impact of positive charge on the chemical shifts in $\mathbf{2} - 2H^+$ is relatively less than is the case for $\mathbf{1} + 2H^+$. To account for the difference in the shielding of benzothiazole protons, we propose that since in the case of $\mathbf{1} + 2H^+$, the proximate benzothizolium rings are ecliptically oriented, they will mutually reinforce the deshielding (downfield shifts) of the protons associated with these ring systems. On the other hand, in $\mathbf{2} - 2H^+$ the positively charged benzothiazolium ring is eclipsed with the neutral benzo-ring in the opposite stack and thus the magnitude of downfield shift of benzothiazolium ring protons should be relatively less. Alternatively, this result can also be interpreted by invoking the presence of through-space charge transfer from the neutral (π-rich) benzo-ring to the positively charged (π-deficient) benzothiazolium ring in $\mathbf{2} - 2H^+$. This could slightly offset the effects of positive charge, thereby accounting for the lower downfield shifts in this system. Such intramolecular charge transfer phenomena are reminiscent of a variety of donor–acceptor cyclophanes reported in Ref. [1].

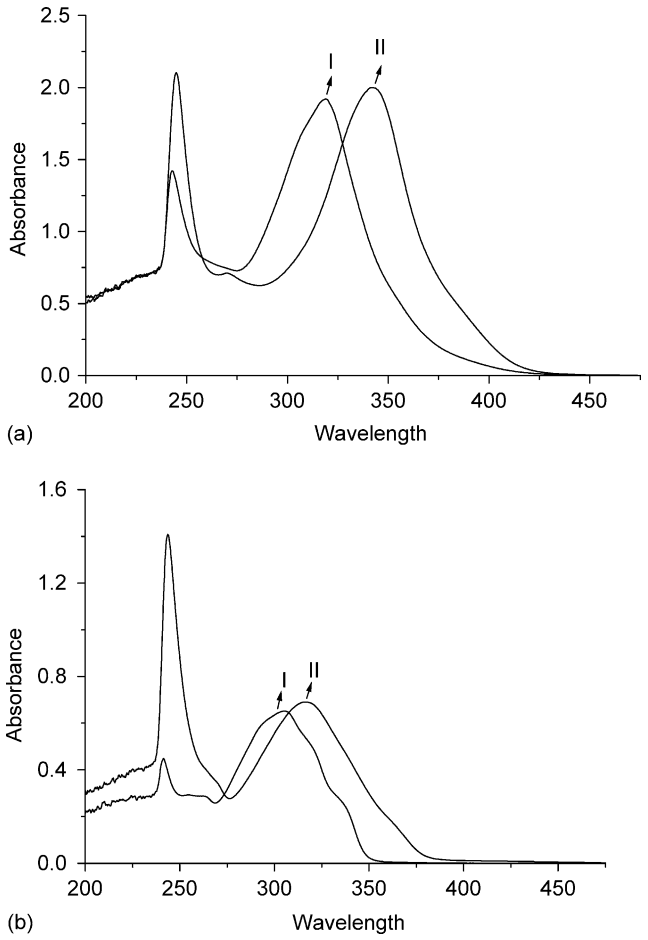


Fig. 1. UV–visible spectra of **1** and **2**: (a) **1** in $CHCl_3$ (I) and 2% TFAA in $CHCl_3$ (II) and (b) **2** in $CHCl_3$ (I) and 2% TFAA in $CHCl_3$ (II).

3.2. Optical spectral properties of *1* and *2*

The absorption and emission properties of **1** and **2** were of interest in view of the facts that (a) these heterophanes possess a donor acceptor, 2-arylbenzothiazole structural motif; and (b) the transannular distance and relative orientation of the chromophores are different in these molecules. The UV–visible spectra of *syn*-**1** and *anti*-**2** recorded in chloroform solvent (Fig. 1) showed λ_{max} at 317 nm (ε_{max} 2.8×10^{-4}) and 305 nm (ε_{max} 3.1×10^{-4}), respectively, while for the reference compound, PBT the λ_{max} appears at 299 nm (ε_{max} 2.1×10^{-4}) [23]. The observed bathochromic shifts for **1** and **2** in comparison to the model PBT may be attributed at least in part to transannular $\pi-\pi$ interaction [24]. On the other hand, marked difference in the λ_{max} values between **1** and **2** could be a consequence of varying degree of through-bond vs. through-space charge transfer interactions, which in turn could differently affect the excitation energies in these molecules. Addition of 2% TFAA in $CHCl_3$ solution induces a bathochromic shifts in the absorption maxima by 25 nm (λ_{max} at 342 nm) and 19 nm (λ_{max} at 324 nm) for **1** and **2**, respectively. The model system, PBT in $CHCl_3$-TFAA solvent exhibits a red shift of 21 nm (λ_{max} at 320 nm) [23]. These red shifts most likely arise from increased charge transfer interaction due to enhanced acceptor property of the N-protonated benzothiazole moieties compared to the parent, neutral systems.

The emission spectra of **1** and **2** are shown in Fig. 2. When excited at its absorption wavelength at 317 nm, **1** in $CHCl_3$ showed a structureless emission at 440 nm registering a Stokes shift of 127 nm. For the *anti*-bislactone **2**, when excited at 305 nm, a single structureless emission occurs at 369 nm with a Stokes shift of just 69 nm. For the model, PBT, the emission occurs at 375 nm (λ_{ex} at 315 nm) with a Stokes shift of 60 nm. Despite the fact that the emission bands in heterophanes **1** and **2** are broad and structureless, these emissions are unlikely to be due excimer/exciplex formation on the ground that (a) even in the reference PBT, we observe a similar broad, structureless emission; and (b) the emissions are not quenched in the presence of oxygen; and (c) no literature precedent seems to exist for 2-arylbenzothiazole systems exhibiting excimer type emissions. We, therefore propose that the emissions in **1** and **2** are most likely originating from a locally excited state (S1 $\rightarrow$ S0). A considerably large Stokes shift of 127 nm for **1** in comparison to both *anti*-**2** and the model PBT suggests that the emission in **1** takes place from a highly relaxed,

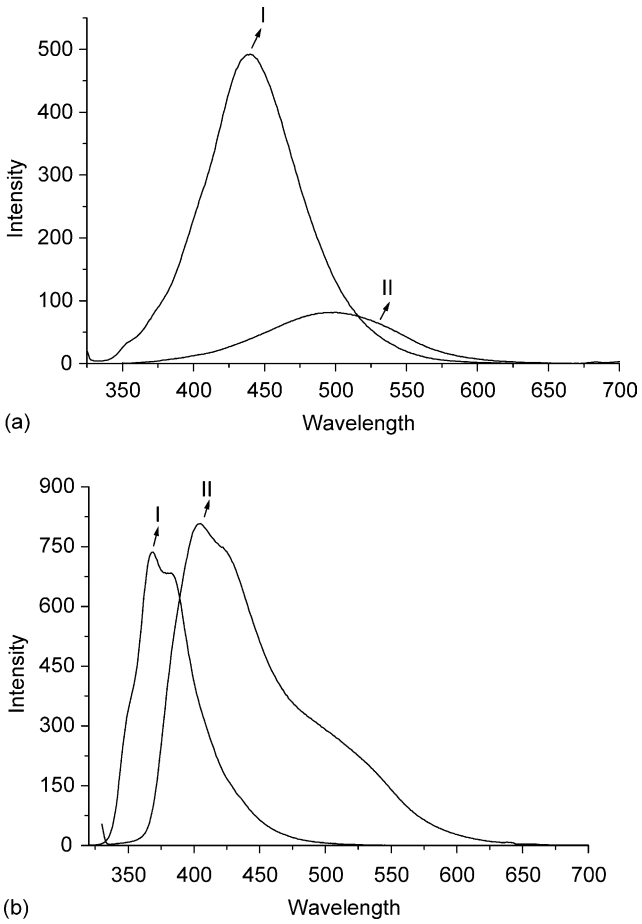
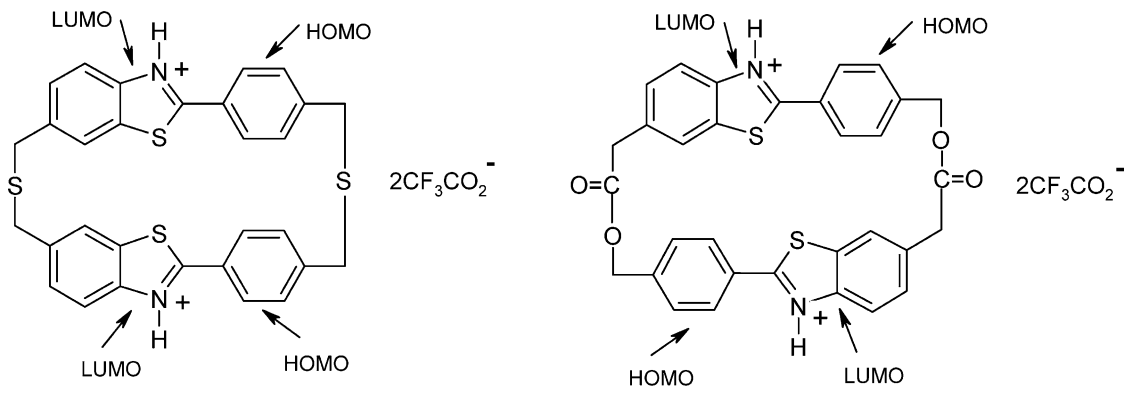


Fig. 2. Emission spectra of **1** and **2**: (a) **1** in $CHCl_3$ (I) and 2% TFAA in $CHCl_3$ (II) and (b) **2** in $CHCl_3$ (I) and 2% TFAA in $CHCl_3$ (II).

equilibrated S1 excited state, i.e. Frank–Condon state [26]. This may be rationalized in terms of relatively rigid nature of **1** that might allow rapid reorganization of the solvent molecules to stabilize the excited state structure. For the case of relatively less strained **2** (and the model PBT) entailing greater conformational flexibility, solvent reorganization accompanying the excited state could be a relatively less efficient process, resulting in less pronounced Stokes shifts. Furthermore, nearly similar values of the Stokes shifts for **2** and the model PBT (69 and 60 nm) indicate similar excited state structures in these molecules [25].

In $CHCl_3$–TFAA, a single emission band believed to be from a locally excited state for **1** appeared at 498 nm upon excitation at 342 nm. The red shift for the emission band in **1** in the presence of TFAA compared to the neutral solution is in accord with the red shift also observed in its absorption spectrum (Fig. 1). In contrast to **1**, bislactone-**2** exhibited a dual emission, a strong higher energy emission (λ_{em} 405 nm) appears to be due to a locally excited state (S1 → So), whereas a broad low intensity emission band located at longer λ (503 nm) is proposed to occur from an intramolecular charge transfer excited state (CT → So). It is noteworthy that in 2-arylbenzothiazole systems, both the HOMO and LUMO are reported to be located on the aryl ring with the benzothiazole moiety serving as a substituent [23b]. Though, such may be the case in the neutral 2-aryl benzothiazole systems, in the presence of TFAA, we presume that the LUMO shifts position from the aryl ring to the protonated, electron deficient benzothiazolium ring. However, the HOMO is expected to retain its position on the aryl ring, as illustrated in Chart 1. Accordingly, for bislactone-**2**, due to the eclipsed orientation of donor and acceptor rings, intramolecular charge transfer from the HOMO of one chromophore to the LUMO of the another chromophore across space appears eminently feasible. Thus, in addition to the local emission, the presence of a new longer wavelength emission in **2** can be reasonably accounted for due to the charge transfer emission (CT → S0). In contrast, in **1** the donor and the acceptor components in the opposite stacks are oriented obliquely from each other thereby precluding effective HOMO–LUMO interaction through space. Thus, on this premise the presence of only local emission with the complete exclusion of charge transfer emission in **1** is understandable. It is noteworthy that the emission band **1** in the presence of TFAA was of much reduced intensity compared to that observed for **2** (Fig. 2). Relatively, higher molecular



1+2H$^+$ **2**+2H$^+$

Chart 1. Proposed HOMO–LUMO assignments.

Table 2
Stable conformations and energies of **1** and **2** by MM2 calculations

Dithia-1			Bislactone-2		
Conformers	ΔE in kJ/mol	Interring distance CH_2-CH_2 (Å)	Conformers	ΔE in kJ/mol	Interring distance CH_2-CH_2 (Å)
Syn–syn (a)	28.7	2.81	*Syn–syn* (a)	296.7	3.59
Anti–anti	28.7	2.81	*Anti–anti*	296.7	3.59
Syn–anti	28.7	2.81	*Syn–anti*	297.8	3.61
Anti–syn	29.0	2.81	*Anti–syn*	301.4	3.59
Syn–syn (b)	29.8	2.81	*Syn–syn* (b)	301.4	3.60

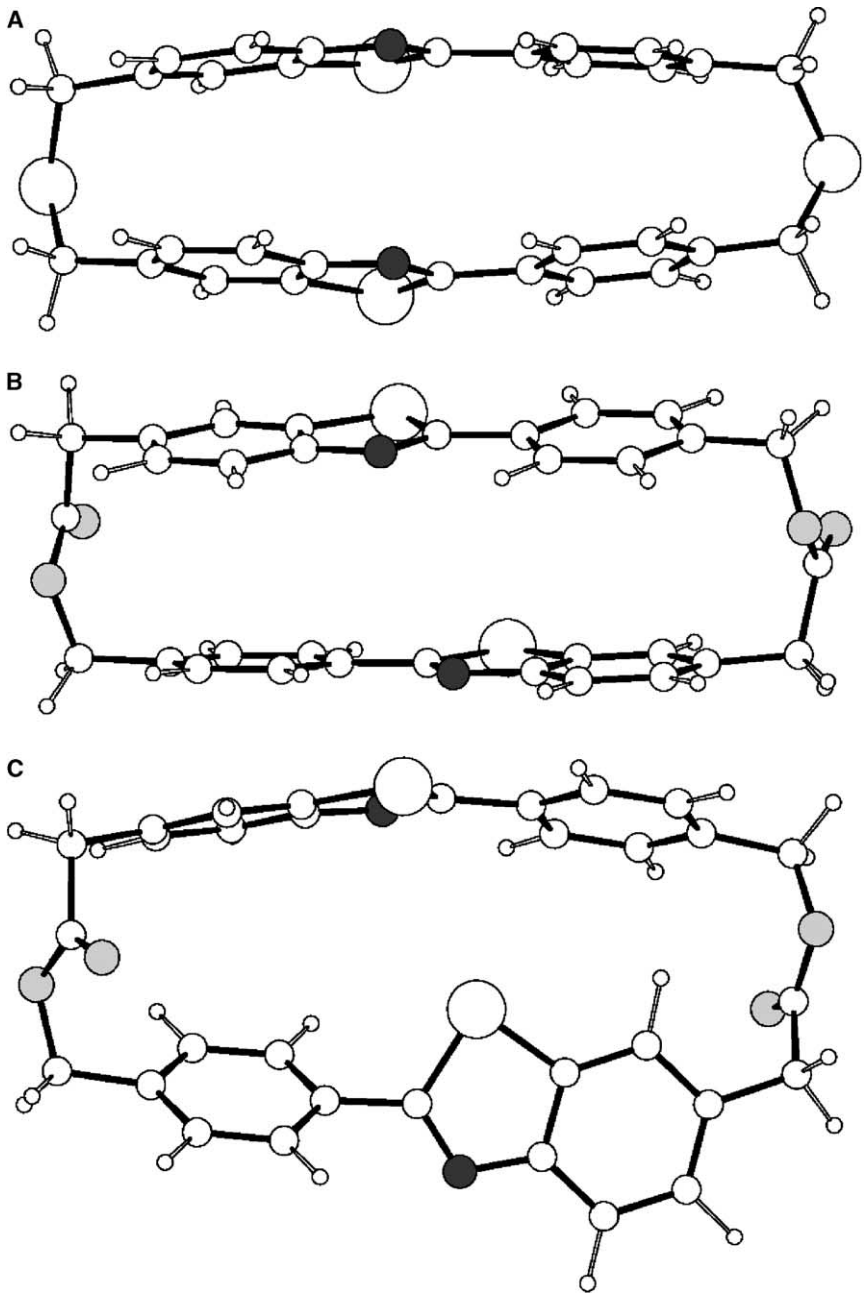


Fig. 3. Selected computer generated conformations: *syn–syn* **1**(A), *syn–syn* **2** (B), and a higher energy conformation of **2** (C).

strain in **1** could contribute to internal quenching in this molecule [27].

3.3. Molecular modelling of *1* and *2*

Since, the thiazole nucleus is unsymmetric owing to 1,3-disposition of two different heteroatoms, possibility exists for the presence of many conformations of **1** and **2** depending upon the relative orientation of two aryl-benzothiazole stacks. Since, crystals of **1** and **2** were unsuitable for single X-ray crystallographic structural analysis, we carried out molecular modelling to probe the conformational aspects of these systems. Two thousand conformations of **1** and **2** were generated by random search Monto Carlo method [28] and optimized by PRCG Conjugated Gradient molecular mechanics minimization method [29] using the Macromodel (version 5.5) program [30] with the MM2 force field [31] and GB/SA chloroform solvation [32]. From these conformational searches, all possible conformations within 12 kcal/mol from the global minima were analyzed. In both cases, we are able to get five stable conformations within 5 kcal/mol from the global minimum. The difference between these five conformers is the relative orientation of the heteroatoms in the bridges and in the thiazole rings. The first designation (*syn* or *anti*) refers to the orientation of the heteroatoms (S or lactone C=O) in the bridges. The second designation corresponds to the orientation of the heteroatoms in the thiazole rings. The third designation (a or b) for *syn–syn* indicates that the sulfur atoms in the thiazole ring have the same (or opposite) orientation with respect to those of sulfur atoms in **1** or the lactone carbonyl in **2** in the bridges. The corresponding steric energies ΔE are presented in Table 2 and for illustration, only *syn–syn* conformers for **1** and **2** are shown in Fig. 3.

Low energy differences between the five most stable conformations clearly suggest no particular bias for any of the *syn*/*anti* forms of **1** and **2**. The comparison of geometries of five conformers of **2** reveals that aryl-benzothiazole components are oriented nearly parallel with interring separation of ca. 3.6 Å. The transannular gap appears to be sufficiently large in **2** to allow for unhindered ring rotations through the *phane* cavity. Further, we also obtain a higher energy conformation in **2** (*E* 301 kcal/mol, Fig. 3C) in which rings in one stack are nearly perpendicular with respect to those in the opposite stack. This particular conformation resembles the transition state during the ring inversion process, a feature, which lends supports to the possibility of ring rotation in this molecule. For the case of **1**, the frame in various conformations is slightly curved with interring separation of ca. 2.8 Å. Relatively, closely spaced chromophores in **1** support higher magnitude of shielding and transannular interaction as discussed earlier.

On the basis of dynamic NMR analysis, we have concluded the presence of free bridge inversions in heterophanes **1** and **2**. However, whether rings are rotating or not could not be settled since the ^{1}H NMR spectra were found to be temperature independent up to +120 °C. The presence of a single set of well resolved signals in the ^{1}H NMR spectra of both **1** and **2**, and rather low energy differences between various reasonable conformations (Table 2) lead us to speculate that these molecules probably exist as time-averaged, freely interconverting conformations. Indeed, literature reports several examples of [3.3] [33] and [4.4] type cyclophanes [34] exhibiting free conformational rotations. Nevertheless, due to constricted cavity (ca. 2.8 Å), the energy barriers to conformational inversions in **1** can be assumed to be higher compared to **2** which possesses a relatively larger cavity dimension (ca. 3.6 Å).

4. Conclusion

In the present work, we have reported for the first time incorporation of photoemittive benzothiazole heteronuclei into the cyclophane framework in the form of structures **1** and **2**. The dynamic ^{1}H NMR spectra of **1** and **2** were found to be temperature independent from −55 to +120 °C thus suggesting the presence of free conformational rotation in these systems. The importance of the relative orientation of the benzothiazole chromophores in **1** and **2** was borne out by optical spectra, in particular the fluorescence spectra data. The short bridged dithia-**1**, having the *syn* orientation of aryl-benzothiazole components showed both in the neutral and acidic conditions only a single emission arising from the locally excited state. However, bislactone-**2** having *anti* oriented aryl-benzothiazole chromophores displayed under acidic condition a dual emissions; a higher energy band is assigned to a locally excited emission, whereas a broad, lower energy emission is believed to be originating from an intramolecular charge transfer interaction. This is a consequence of eclipsed orientation of donor phenyl ring and the acceptor benzothiazolium ring in the opposite stacks. The HOMO–LUMO interaction has been proposed to explain the disparity in the emission behavior of heterophanes **1** and **2**. Along expected lines, the energy minimization indicted the short bridged **1** to be relatively more strained compared to the longer bridged **2**. On the basis of dynamic ^{1}H NMR analysis coupled with the molecular modelling, we speculate that both **1** and **2** exist as time averaged conformations. Work is in progress to synthesize [2.2] *syn*- and [2.2] *anti*-phenyl benzothiazolophanes to more closely examine the effects of chromophoric orientations on conformational and photophysical properties.

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