

# The synthesis of novel benzocyclobutene monomers containing the squaric acid unit

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Several novel benzocyclobutene monomers containing squaric acid unit have been synthesised. They were characterised by IR, <sup>1</sup>H NMR, MS, UV-vis and have been element analyses and some have potential applications in polymer type organic electroluminescent materials.

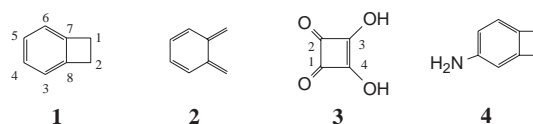
**Keywords:** benzocyclobutene, squaric acid, squaraines, electroluminescent material monomers

Benzocyclobutene (BCB, **1**) is a very useful starting material for organic synthesis<sup>1</sup> and for high-performance polymer materials.<sup>2</sup> When heated to about 200°C, the cyclobutane ring of BCB opens to form the highly reactive *o*-quinodimethane intermediate **2**, which can undergo Diels–Alder reactions with dienophiles and forms polymers.<sup>3</sup> The polymers have been widely used in the microelectronics industry<sup>4</sup> in electronics packing applications due to their low dielectric constants, low water uptake, high thermostability and ease of processing. Squaric acid, **3** (3,4-dihydroxy-3-cyclobutene-1,2-dione) and its derivatives are important organic materials.<sup>5</sup> The optical characteristics of the squaraines<sup>6</sup> have made them very attractive for a number of industrial applications, *e.g.* xerography, in photoreceptors, in organic solarcells, as electroluminescent materials and in optical recording.

In order to explore the novel high performance polybenzocyclobutene electroluminescent materials, this paper reports the design, synthesis and characterisation of novel benzocyclobutene monomers containing the squaric acid unit. These monomers include one or two BCB groups, and are yellow to purple. The monomers (*e.g.* **5**, **8**, **11** and **12**) are easy to copolymerise with unsaturated units (*e.g.* monomers, oligomers or soluble polystyrene) or to polymerise with themselves and form a large group of polymers. They can be polymerised directly at the surface of a device at 200–250°C without destroying the other parts and no small molecule byproducts are produced. This is very important in the production of electronic devices. Furthermore, the squaraines have high decomposition temperatures (>300°C). The polymerisation of BCB monomers does not destroy the four-member ring of the squaraines and so we expected that they may be useful in polymer type organic electroluminescent materials.

## Results and discussion

1,3-bis (*N*-benzocyclobuten-4'-yl-amino)squaraine **5** was prepared by amidation of squaric acid **3** with 2.1 equiv

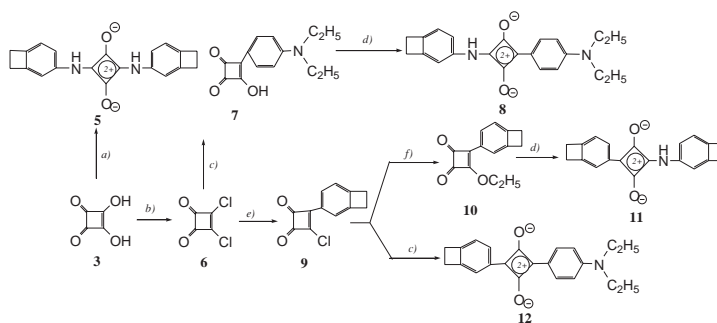


**Scheme 1**

4-aminobenzocyclobutene **4** (4-AminoBCB) in dry butanol (Scheme 2). We used 3,4-dichloro-3-cyclobutene-1,2-dione **6** (squaric dichloride) as the acylation reagent, and synthesised several acylation products of BCB **7**, **9** and **12**. 1-[*p*-(Diethylamino)phenyl]-3-(*N*-benzocyclobuten-4'-yl-amino)squaraine **8** was synthesised by the amidation of 3-[*p*-(diethylamino)phenyl]-4-hydroxy-3-cyclobutene-1,2-dione **7**, which was prepared also under the conditions of a Friedel–Crafts reaction with *N,N*-diethylaniline. Aminolysis of 3-(4'-benzocyclobutenyl)-4-ethoxy-3-cyclobutene-1,2-dione **10** by 4-AminoBCB **4** in butanol yielded 1-(4'-benzocyclobutenyl)-3-(*N*-benzocyclobuten-4'-yl-amino) squaraine **11**.

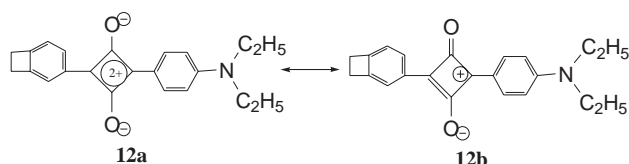
The <sup>1</sup>H NMR spectra of **8** and **11** exhibit no N–H proton signals, which was due to the <sup>14</sup>N quadrupole moment effect and the speed of exchange of the N–H protons. The chemical shift of the methylene protons in the BCB group was at lower field by 0.03–0.27 ppm than those of the methylene protons of the 4-AminoBCB group. The former protons give a singlet and the latter a doublet. The stronger the electron withdrawing effect, the lower field is the chemical shift.

The IR spectrum of **5** exhibits a strong absorption band at ~1584 cm<sup>-1</sup>. The absence of C=O stretching indicates that the C–O bond has very little double bond character and that the  $\pi$ -electrons are fully delocalised in the central C<sub>4</sub>O<sub>2</sub> unit. The IR spectrum of **12** shows strong absorptions at ~1730 cm<sup>-1</sup> and ~1600 cm<sup>-1</sup>, which suggests that the C–O bonds have some double bond character and the  $\pi$ -electrons are not fully delocalised in the central C<sub>4</sub>O<sub>2</sub> unit. In the IR spectra of **8** and



**Scheme 2** (a) 2.1 equiv 4-aminoBCB **4**, butanol, 90–100°C, 3 h; (b) 2.1 equiv SOCl<sub>2</sub>, cat. amount DMF, reflux for 2 h; (c) 1.1 equiv *N,N*-diethylaniline, 1.5 equiv AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (d) 1.1 equiv 4-AminoBCB **4**, butanol, 90–100°C, 3 h; (e) 1.1 equiv BCB, 1.5 equiv AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (f) ethanol, reflux for 6 h.

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Scheme 3

**11**, single weak C=O absorption band at  $\sim 1770\text{ cm}^{-1}$  and strong absorption bands of the delocalised  $\text{C}_4\text{O}_2$  unit ( $\sim 1580\text{ cm}^{-1}$  and  $1612\text{ cm}^{-1}$ ) indicate that the C=O double bond character has become to very weak. Comparing the IR spectra of **8** and **11** with those of **12** or **5**, the delocalisation extent of the  $\pi$ -electrons in the central  $\text{C}_4\text{O}_2$  unit of **8** and **11** is greater than that of **12** and less than that of **5**. The resonance (**12**  $\longleftrightarrow$  **12b**) – (Scheme 3) is important for **12**.

The UV-vis spectra of **8**, **11** and **12** show that the  $\lambda_{\text{max}}(\text{CHCl}_3)$  positions are at 508, 442 and 496 nm, respectively which is very important for their applications as functional materials.

In summary, some novel benzocyclobutene monomers containing the squaric acid unit have been synthesised. These monomers have potential applications in polymer type organic functional materials. Studies of the properties of the polymers are in progress.

## Experimental

Melting points were taken on a micro-melting point apparatus (uncorrected).  $^1\text{H}$  NMR spectra were recorded on an Avance Bruker-300 instrument and chemical shifts in ppm reported with TMS as the internal standard. MS were measured on a Finnigan MAT4510 instrument. Elemental analyses were performed on a Carlo Erba 1106 instrument. IR spectra were obtained with a Perkin-Elmer 16 PC FIT-IR spectrophotometer. UV-vis spectra were recorded on TU-1901 UV-vis Spectrophotometer. Benzocyclobutene **1**, **7**, 4-aminobenzocyclobutene **3**<sup>8</sup> and squaric acid **4**<sup>9</sup> were prepared according to the literature.

**General procedure for the synthesis of 7, 9, 10 and 12:** To an anhydrous  $\text{AlCl}_3$  (1.39 g, 10.4 mmol) suspension in dry  $\text{CH}_2\text{Cl}_2$  (15 ml) under nitrogen at  $5^\circ\text{C}$ , a solution of BCB (0.80 g, 7.65 mmol) or *N,N*-diethylaniline (1.14 g, 7.65 mmol) and squaric dichloride **6** (1.39 g, 6.95 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10 ml) was added dropwise over 2h. The temperature was held at  $5^\circ\text{C}$  for 2h and then at room temperature for 4h (more anhydrous  $\text{AlCl}_3$  (1.39 g, 10.4 mmol) and *N,N*-diethylaniline (1.14 g, 7.65 mmol) was added to the mixture which was further stirred for 2 h to prepare monomer **12**). After the completion of the reaction, the mixture was added slowly to 10% HCl ice-water (20 ml) and the mixture was then extracted with ether (3 $\times$ 30 ml). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residues were purified by chromatography on silica gel to afford **9** and **12**, and by recrystallisation from water to produce **7**. Anhydrous ethanol (30 ml) was added to the residues from the preparation of **9** and refluxing for 6 h and the solvent was removed under reduced pressure. The residues from this were purified by chromatography on silica gel to afford **10**.

**General procedure for the synthesis of monomers 5, 8 and 11:** A suspension of **3** (67 mg, 0.59 mmol), **7** (227 mg, 1.13 mmol) or **10** (257 mg, 1.13 mmol) containing **4** (147 mg, 1.24 mmol) in dry butanol (15 ml) was stirred and held at  $90\text{--}100^\circ\text{C}$  under a nitrogen atmosphere for 3 h. After the mixture had cooled to room temperature, the precipitated squaraine **5** was separated by filtration and washed with butanol (5 ml),  $\text{CHCl}_3$  (5 ml) and  $\text{CH}_3\text{OH}$  (5 ml). The purple precipitated squaraine **8** was isolated by filtration and recrystallised from ethanol. The orange solid **11** was purified by filtration and washed with butanol and petroleum ether.

**1, 3-bis(*N*-benzocyclobuten-4'-yl-amino)squaraine 5:** Yellow solid, yield 90%. m.p.  $>300^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ): 3.11(d, 8H,  $J=4.0\text{ Hz}$ ,  $\text{CH}_2\text{CH}_2$ ); 7.04–7.60 (m, 6H, ArH); 11.22(br., 1H, NH); MS ( $m/z$ , %): 316 ( $\text{M}^+$ , 30). IR (KBr,  $\text{cm}^{-1}$ ): 1564 (Vs). Anal. Calcd. For  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$ : C, 75.93; H, 5.10; N, 8.86; Found: C, 75.39; H, 5.26; N, 8.66.

**1-[*p*-(diethylamino)phenyl]-3-(*N*-benzocyclobuten-4'-yl-amino)squaraine 8:** Purple crystal, yield 82%. m.p.  $>300^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.25 (t, 6H,  $J=7.1\text{ Hz}$ ,  $\text{CH}_3$ ); 3.20 (d, 4H,  $J=5.5\text{ Hz}$ ,  $\text{CH}_2\text{CH}_2$ ); 3.48 (q, 4H,  $\text{CH}_2$ ); 6.72 (d, 2H,  $J=9.2\text{ Hz}$ ); 7.10 (d, 1H,  $J=8.2\text{ Hz}$ , ArH); 7.69 (d, 1H,  $J=7.6\text{ Hz}$ , ArH); 7.90 (s, 1H, ArH); 8.24 (d, 2H,  $J=9.1\text{ Hz}$ , ArH); MS ( $m/z$ , %): 346 ( $\text{M}^+$ , 28); IR (KBr,  $\text{cm}^{-1}$ ): 1783(w), 1579(Vs).  $\lambda_{\text{max}}$

( $\text{CHCl}_3$ ): 508 nm. Anal. Calcd. For  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$ : C, 76.28; H, 6.40; N, 8.09; Found: C, 76.12; H, 6.42; N, 8.06.

**3-(4'-benzocyclobutenyl)-4-chloro-3-cyclobutene-1,2-dione 9:** Petroleum ether / ethyl acetate (15:1 by vol) eluent produced yellow crystals **9**, yield 40%. m.p.  $128\text{--}130^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 3.30 (s, 4H,  $\text{CH}_2\text{CH}_2$ ); 7.28 (d, 1H,  $J=7.7\text{ Hz}$ , ArH); 7.93 (s, 1H, ArH), 8.16 (dd, 2H,  $J=7.7, 1.3\text{ Hz}$ , ArH); MS ( $m/z$ , %): 218 ( $\text{M}^+$ , 38). IR (KBr,  $\text{cm}^{-1}$ ): 1807(Vs), 1775(Vs).  $\lambda_{\text{max}}(\text{CHCl}_3)$ : 316 nm. Anal. Calcd. For  $\text{C}_{12}\text{H}_7\text{ClO}_2$ : C, 65.92; H, 3.23; Cl, 16.22; Found: C, 66.00; H, 3.37; Cl, 15.89.

**3-(4'-benzocyclobutenyl)-4-ethoxy-3-cyclobutene-1,2-dione 10:** Petroleum ether/ethyl acetate (10:1 by vol) eluent afforded yellow needle crystal **10**, yield 36%. m.p.  $130\text{--}132^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.58 (t, 3H,  $J=7.1\text{ Hz}$ ,  $\text{CH}_3$ ); 3.25 (s, 4H,  $\text{CH}_2\text{CH}_2$ ); 4.96 (q, 2H,  $\text{CH}_2$ ); 7.20 (d, 1H,  $J=7.5\text{ Hz}$ , ArH); 7.74 (s, 1H, ArH); 7.96 (dd, 1H,  $J=7.6, 1.2\text{ Hz}$ , ArH); MS ( $m/z$ , %): 228 ( $\text{M}^+$ , 38); IR (KBr,  $\text{cm}^{-1}$ ): 1782(Vs), 1742(Vs).  $\lambda_{\text{max}}(\text{CHCl}_3)$  1: 328 nm;  $\lambda_{\text{max}}(\text{CHCl}_3)$  2: 315 nm. Anal. Calcd. For  $\text{C}_{14}\text{H}_{12}\text{O}_3$ : C, 73.67; H, 5.30; Found: C, 73.56; H, 5.35.

**1-(4'-benzocyclobutenyl)-3-(*N*-benzocyclobuten-4'-yl-amino)squaraine 11:** Orange solid, yield 80%. m.p.  $>300^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 3.23 (t, 4H,  $J=2.8\text{ Hz}$ ,  $\text{CH}_2\text{CH}_2$ ); 3.26 (s, 4H,  $\text{CH}_2\text{CH}_2$ ); 7.16 (d, 1H,  $J=8.8\text{ Hz}$ , ArH); 7.20 (d, 1H,  $J=7.9\text{ Hz}$ , ArH); 7.82 (d, 1H,  $J=7.8\text{ Hz}$ , ArH); 7.93 (s, 1H, ArH); 7.97 (s, 1H, ArH); 8.25 (dd, 1H,  $J=8.8, 1.2\text{ Hz}$ , ArH); MS ( $m/z$ , %): 301 ( $\text{M}^+$ , 15); IR (KBr,  $\text{cm}^{-1}$ ): 1772(w), 1612(Vs).  $\lambda_{\text{max}}(\text{CHCl}_3)$  1: 442 nm;  $\lambda_{\text{max}}(\text{CHCl}_3)$  2: 420 nm. Anal. Calcd. For  $\text{C}_{20}\text{H}_{15}\text{NO}_2 \cdot 3/2\text{ H}_2\text{O}$ : C, 73.16; H, 5.52; N, 4.26; Found: C, 73.20; H, 5.15; N, 4.28.

**1-(4'-benzocyclobutenyl)-3-[(*p*-diethylamino)phenyl]squaraine 12:** With  $\text{CHCl}_3$ / petroleum ether (10: 1 by vol) eluent produced red crystals **12**, yield 22%. m.p.  $134\text{--}136^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.27 (t, 6H,  $J=5.6\text{ Hz}$ ,  $\text{CH}_3$ ); 3.29 (s, 4H,  $\text{CH}_2\text{CH}_2$ ); 3.50 (q, 4H,  $\text{CH}_2$ ); 6.92 (s, 2H, ArH); 7.24 (d, 1H,  $J=7.6\text{ Hz}$ , ArH); 7.73 (s, 1H, ArH); 7.94 (d, 1H,  $J=7.6\text{ Hz}$ , ArH); 8.15 (d, 2H,  $J=8.4\text{ Hz}$ , ArH); MS ( $m/z$ , %): 331 ( $\text{M}^+$ , 60). IR (KBr,  $\text{cm}^{-1}$ ): 1746(Vs), 1600(Vs).  $\lambda_{\text{max}}(\text{CHCl}_3)$  1: 496 nm;  $\lambda_{\text{max}}(\text{CHCl}_3)$  2: 270 nm. Anal. Calcd. For  $\text{C}_{22}\text{H}_{21}\text{NO}_2$ : C, 79.73; H, 6.39; N, 4.23; Found: C, 79.43; H, 6.50; N, 4.23.

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