Synthesis of new 2,7-dibromo 9-benzocyclobuten-3-yl-9H-fluorene derivatives - perspective dielectric materials for electronics

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Abstract. The approaches to the synthesis of new derivatives of 2,7-dibromofluorene and benzocyclobutene have been investigated. For this purpose 9-bicyclo [4.2.0] octa-1 (6), 2,4-trien-3-yl-2,7-dibromo-9H-fluoren-9-ol was synthesized by reaction of 2,7-dibromo-fluoren-9-one with 3-benzocyclobutene magnesium bromide. The possibility of reduction and substitution of the hydroxyl group at position 9 of the obtained compound with aromatic substituents under conditions of acid catalysis is demonstrated. Target compounds were obtained in yields from 75 to 90%.

1. Introduction
In recent years, a large number of works, including patents [1-8] has been devoted to the synthesis of derivatives of benzocyclobutene (BCB) and fluorene. Hybrids based on them are used to create polymer functional structures that act as dielectric materials with high thermal stability and excellent dielectric properties. On the contrary, the introduction of polar donor or acceptor fragments (figure 1, 1 [6]) into the structure and the creation of conjugated polymers leads to the appearance of fluorescence properties, hole conductivity, useful for creating a number of electronic devices, including solar panels, polymer electroluminescent materials, displays, etc.

The introduction of a benzocyclobutene fragment into the fluorene structure results in crosslinked highly stable polymers with good insulating properties, mechanical strength, and thermal stability. For example polymer based on monomer 2 [9] (figure 1) showed high values of the dielectric constant (ε~2.7) in the frequency range from 0.15 to 30 MHz and Td5% values equal to 437 ° C and 372 ° C in an atmosphere of nitrogen and air, respectively. The great advantage of such cross-linking is the absence of low molecular weight by-products capable of deteriorating the homogeneity, dielectric, mechanic and optical properties of the final polymers.

Polymerization in these materials occurs by thermally initiated benzocyclobutene ring opening with the formation of active o-xylene 4, which is capable to enter into polymerization,dimerization [4+4] or [4+2] cycloaddition reactions. Depending on the environment, the active o-xylene form of
benzocyclobutene is able to interact either with active double bonds of alkenes (to form 5), or in the absence of such, to form structures 6 or 7 (figure 2).

![Figure 1. Examples of benzocyclobutene containing fluorene structures.](image1)

![Figure 2. Scheme of dimerization and polymerization of BCB derivatives in the presence or absence of double bonds.](image2)

Difficulties in the synthesis of benzocyclobutene derivatives lie in the sensitivity of the cyclobutene ring to acids and the impossibility of carrying out processes at high temperatures. Electrophilic substitution reactions (bromination, acylation etc), proceeding with the release of hydrogen halides, usually lead to the formation of a series of the cyclobutene ring opening by-products [10-19]. Yields in such reactions rarely exceed 50%. (figure 3)

In this work, we demonstrated examples of successive synthesis of a number of 2,7-dibromofluorene and benzocyclobutene derivatives using acid catalysis (MeSO$_3$H, BF$_3$*Et$_2$O). These compounds are of interest as building blocks for the synthesis of monomers for polymers with hole or electron conductivity, electroluminescent materials, etc.

The synthetic route is started from a cheap and affordable product - fluorenone 9, which in the first stage is brominated in qualitative yield, giving a 2,7-dibromo derivative 10. Reaction of 10 with Grignard reagent, obtained from 3-bromobenzocyclobutene and Mg, gives 9-benzocyclobuten-3-yl-9-hydroxy-9H-fluoren-9-ol 12 with a yield of over 90%. The hydroxyl group in the 9-th position of 9-benzocyclobuten-3-yl-9-hydroxy-9H-fluoren-9-ol can be replaced by an aromatic moiety such as benzocyclobuten-3-yl or toluene-4-yl. The approach is based on the formation of a carbocation by the action of boron trifluoride etherate followed by an attack with electron-rich aryl. This method allows to obtain both symmetric and non-symmetric derivatives of fluorene and benzocyclobutene (13, 14) from good to excellent yields. The presented synthesis of structure 13 may seem more attractive in comparison with the known methods, which consists in intermolecular cyclization of bicyclo [4.2.0] octa-1,3,5-trien-3-yl -bicyclo [4.2.0] octa-1 (6), 2,4-trien-3-yl- (4,4'-dibromo-biphenyl-2-yl) -methanol [20]. The presented results provide easy access to useful structures that can be used to develop materials for solar cells, electroluminescent devices, and dielectric materials.
Figure 3. Examples of acid catalysts formation of by-products in electrophilic substitution reaction.

There are many examples in the literature for the preparation of 9H-fluorene, which can be alkylated by aliphatic alkyl halides. The resulting products have better solubility in organic solvents and polymer media.

We found that a suitable method to replace the hydroxyl group of 9-benzocyclobuten-3-yl-2,7-dibromo-9-hydroxy-9H-fluoren-9-ol 12 with a hydrogen atom is the interaction with triethylsilane in the presence of methanesulfonic acid. Yield of reaction was 84%.

All synthesized compounds were characterized by $^1$H, $^{13}$C NMR and HRMS. In all cases, the appearance of benzocyclobutene ring opening products was not observed that demonstrated by the presence of characteristic signals of the cyclobutene ring in the region of 3.15-3.20 ppm (figure 5).
2. Experimental part

NMR spectra were registered using a Bruker AM-300 or a Bruker Avance 600 spectrometer in or CDCl₃ (¹H, 300 or 500 MHz; ¹³C, 75 MHz). High-resolution mass spectra were registered using a Bruker micrOTOF II spectrometer with electrospray ionization (ESI). Analysis of the reaction mixtures to confirm the purity of all products was performed using TLC on the Merck Silicagel 60 F254 UV-254 plates.

2.1 3-Bromobenzocyclobutene (11)
Benzocyclobutene (23.7 g, 22.8 mmol) was dispersed in 240 ml of water at room temperature. After cooling with ice water, 11.7 ml of bromine (-10-5°C) was added dropwise. After complete of addition, the ice and water bath was removed and the reaction mixture was warmed to room temperature and stirred overnight (24 hours). The reaction was monitored by TLC until the starting benzocyclobutene disappeared. The mixture was diluted with 50 ml of n-hexane and sodium sulfite (3 g, 23.8 mmol) was added. Upon completion of the addition, the mixture was stirred at room temperature for 30 minutes. In this case, the mixture is discolored. Then, the separated organic layer was dried over anhydrous sodium sulfate, filtered to remove a drying agent, and concentrated under reduced pressure to obtain 3-bromobicyclo[4.2.0]octa-1,2,4-triene. After distillation at 110-114 °C, 28-30 g was obtained as a colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, J = 7.8 Hz, 1H), 7.26 (s, J = 7.0 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 3.31–3.10 (m, 4H).

2.2 2,7-Dibromofluorenone (10)
Br₂ (8.5 ml, 165.2 mmol) was added to a solution of fluorenone (10.00 g, 55.40 mmol) in H₂O (140 ml) for 10 minutes at 0 °C, then heated to 80 °C and stirred for 10 hours. The reaction mixture was cooled to room temperature and additional H₂O (150 ml) was added, followed by a saturated solution of Na₂SO₃ (150 ml). The crude residue was filtered and washed with water to obtain a solid yellow product (18 718 g, 100%). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 1.8 Hz, 2H, COCCH), 7.63 (dd, J = 7.9, 1.8 Hz, 2H, CBrCHCH), 7.39 (d, J = 7.9 Hz, 2H, CBrCHCH); MS (EI+) m / z 336, 338, and 340 (M).

2.3 Synthesis of 9-benzocyclobuten-3-yl-2,7-dibromo-9H-fluoren-9-ol (12)
Solution 1 (Grignard reagent). 12 g of bromobenzocyclobutene (0.065 mol) was added dropwise to 2 g (0.083 mol) of magnesium in 60 ml of dry THF at such a rate that the temperature was 25-40 °C. After addition was complete, the mixture is stirred at 32-34 °C for 1 hour.
Solution 2. In another flask equipped with a thermometer, mixture of 16.9 g (0.05 mol) of dibromofluorenone and 100 ml of THF was prepared. The Grignard reagent (solution 1) was added in small portions at 5°C. The solution darkened, and the precipitate dissolved. After the addition is complete, the mixture is allowed to warm to room temperature and leave overnight. The next day, an abundant precipitate of white color is observed. The mixture was diluted with water. The mixture was extracted with ethyl acetate, evaporated and washed with hexane. The target product was obtained with a yield of 90% \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.51 (s, 4H), 7.45 (s, 2H), 7.21 (d, \(J = 7.7\) Hz, 1H), 7.05 (s, 1H), 6.99 (d, \(J = 7.7\) Hz, 1H), 3.15 (s, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 152.40, 145.96, 145.48, 140.20, 137.45, 132.33, 128.27, 123.75, 122.55, 122.52, 121.54, 119.63, 83.68, 77.45, 77.03, 76.61, 31.60, 29.48, 29.43, 22.70, 22.67, 14.15, 14.12. HRMS, Found 442.9359, Calculated: 442.1531.

2.4 9-Bicyclo [4.2.0] octa-1 (6), 2,4-trien-3-yl-2,7-dibromo-9H-fluorene (15)

The 14 ml of toluene and 1.62 g of triethylsilane were added to 1.42 ml of boron trifluoride etherate was added dropwise to the mixture of 4.42 g of the 9-benzo[cyclobutene-3-yl-2,7-dibromo-9H-fluoren-9-ol. The mixture is heated to 60-70 °C and 1.34 g of methanesulfonic acid was added dropwise over 10 minutes. After completion of the reaction (TLC control, approximately 30 min is required), the mixture is poured into water, washed with Na$_2$CO$_3$ solution, and extracted with ethyl acetate, evaporated and washed with hexane. The target product was obtained in yields from 75 to 90%. The white solid product is poured with hexane, stirred vigorously and filtered. The yield is 3.6 g or 70%.

2.5 Synthesis of 2,7-dibromo-9,9-di (benzocyclobutene-3-yl) -9H-fluorene(13)

1.24 ml of boron trifluoride etherate was added dropwise to the mixture of 4.42 g of the 9-benzo[cyclobutene-3-yl-2,7-dibromo-9H-fluoren-9-ol 12, 1.1 g of benzocyclobutene and 25 ml of methylene chloride at a temperature of -10-0 °C. The mixture was stirred for another 10 minutes, diluted with water (2 ml) and neutralized with a Na$_2$CO$_3$ solution. The organic layer was separated, dried over Na$_2$SO$_4$, filtered through a small layer of silica gel and evaporated on a rotary evaporator. The white solid product is poured with hexane, stirred vigorously and filtered. The yield was 4 g or 75%. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.1\) Hz, 2H), 7.52 (s, 2H), 7.48 (dd, \(J = 8.1, 1.6\) Hz, 2H), 7.03 (d, \(J = 7.8\) Hz, 2H), 6.95 (d, \(J = 7.8\) Hz, 2H), 6.83 (s, 2H), 3.13 (s, 8H). The product is poorly soluble in acetone, ethanol, methylene chloride, soluble in toluene, moderately in THF and poorly soluble in hexane. HRMS, Found 528.9985, Calculated: 528.9986.

2.6 Synthesis of 9- (benzocyclobutene-3-yl) -9- (toluen-4-yl) -2,7-dibromo-9H-fluorene (14)

1.42 ml of boron trifluoride etherate was added dropwise to the mixture of 4.42 g of the 9-benzo[cyclobutene-3-yl-2,7-dibromo-9H-fluoren-9-ol 12, 1 g of toluene and 25 ml of methylene chloride at a temperature of -10-0 °C. The mixture was stirred for another 10 minutes, diluted with water (2 ml) and neutralized with a Na$_2$CO$_3$ solution. The organic layer was separated, dried over Na$_2$SO$_4$, filtered through a small layer of silica gel and evaporated on a rotary evaporator. The white solid product is poured with hexane, stirred vigorously and filtered. The yield is 3.6 g or 70%.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 8.0\) Hz, 2H), 7.48-7.51 (m, 4H), 7.08 (m, 4H), 7.02 (d, \(J = 7.7\) Hz, 1H), 6.95 (d, \(J = 7.8\) Hz, 1H), 6.83 (s, 1H), 3.19 - 3.08 (m, 4H), 2.33 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 153.55, 145.83, 144.71, 143.28, 141.76, 137.98, 137.91, 136.74, 136.71, 136.71, 130.75, 129.44, 129.16, 127.91, 126.74, 122.54, 122.18, 121.80, 121.48, 77.43, 77.00, 76.58, 65.78, 29.51, 29.31, 20.94. HRMS, Found 516.9985, Calculated: 516.9986.

3. Conclusions

In summary, we have successfully synthesized new monomers based on 2-7-dibromofluorenone and benzocyclobutene. Target compounds were obtained in yields from 75 to 90%. We demonstrated the
applicability of the known methods for modifying benzocyclobutene containing fluorene derivatives. The presented results provide easy access to useful structures that can be used to develop materials for solar cells, electroluminescent devices, and dielectric materials. Obtained monomers have a potential application as dielectrics in microelectronic industry.

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