

Short Note

2-(Bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-adamantan-2-ol

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Abstract: A new adamantan-2-ol with a 2-bicyclo[4.2.0]octa-1,3,5-trien-3-yl substituent in the position 2 was synthesized via two stage synthesis starting from benzocyclobutene and adamantan-2-one. The structure of the title compound was determined using ¹H- and ¹³C-NMR, HRMS and XRD.

Keywords: benzocyclobutene; Grignard reaction; 2-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-adamantan-2-ol

1. Introduction

Adamantanes are used in various fields of science such as material chemistry and medicine. Their inclusion into polymer structure gives materials with excellent properties. For example, adamantan-1-yl acrylate, methacrylate, and 1-vinyl-adamantane-based polymers and polymers containing pendant diamondoid moieties (adamantane and diamantane) are soluble, colorless polymers with an unusual combination of moderately high refractive index (1.48–1.60) and low optical dispersion [1]. These properties make the polymers valuable as optical plastics for lenses, viewfinders, data storage media, light-diffusing elements, etc. [1] It was found that the introduction of adamantyl moieties in poly(1-adamantyl acrylate) increase thermal stability of the polymer in comparison with poly(methyl methacrylate) (PMMA) [2]. A similar result was obtained for 1,3-bis(4-phenyl)adamantane based polysiloxane **P1** [3] that has thermal stability (T_{d5}) higher than 520 °C in N₂. Introduction of adamantyl moieties in polymer chain in 1,3-bis(4-phenyl)adamantane based polysiloxane **P1** also increases glass transition temperature (T_g) to 105–115 °C, more than 125 °C higher than that of poly(tetramethyl-1,4-silphenylenesiloxane) analog [3].

Adamantyl is a non-polar substituent, which should contribute to the improvement of dielectric properties in polymers. This is a very useful characteristic for insulation materials. The development of microelectronics requires high performance interlevel dielectric materials with an extremely low dielectric constant and loss factor.

Adamantane and benzocyclobutene (BCB)-based polymer materials have attracted significant attention because of their low-dielectric constant, low loss factor, and excellent high-temperature performance. An example of such material is **AdaDBDVS** [4]. **AdaDBDVS** has $T_g = 350$ °C, $T_{d5\%} = 449$ °C and dielectric constant (K) = 2.78.

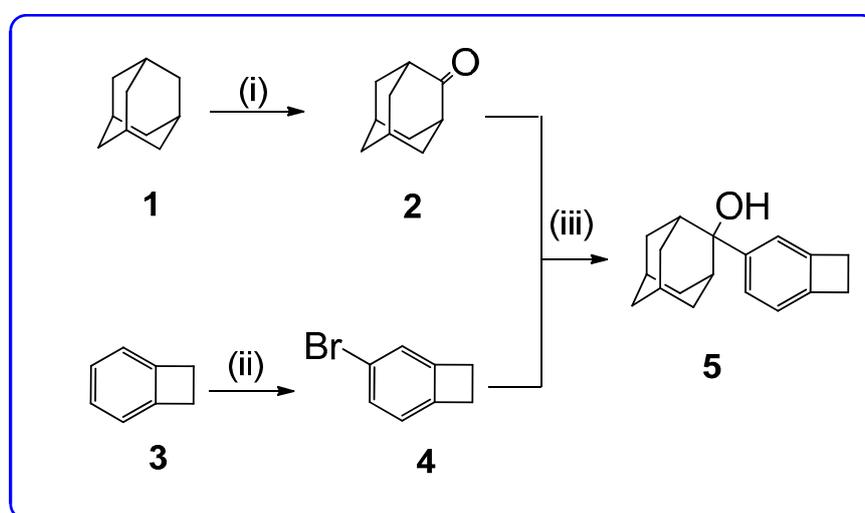
The combination of benzocyclobutene and adamantane in a monomer or polymer seems attractive because a benzocyclobutene ring opens when heated above 200 °C and gives an active isomer (o-xylylene) that provides crosslinking of the polymer. BCB crosslinked polymers have high values of

glass transition temperatures (that is relatively low for linear, non-crosslinked adamantane polymers) and high thermal stability [5–7].

In this study, we synthesized benzocyclobutyl and adamantyl containing hybride molecule—(2-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-adamantan-2-ol) (**5**), which have free alcohol groups for further modifications. The obtained material can be useful for the developments of new materials with good thermal stability and dielectric properties.

2. Results and Discussion

Synthesis of the title compound is presented in Scheme 1 and includes a three-stage process starting from adamantane (**1**) and benzocyclobutene (**3**). Adamantan-2-one (**2**) was obtained from **1** by oxidation by hot sulfuric acid for 25 h [8]. 4-Bromobenzocyclobutene (**4**) was obtained from **3** by bromination in water solution [9–11]. A reaction of adamantan-2-one (**2**) with a Grignard reagent synthesized from **4** gave **5** with 70% yield.



Scheme 1. Synthesis of **5**. (i) H_2SO_4 , heating, 25 h; (ii) Br_2 , H_2O , -10 – 20 °C, 20 h; (iii) (a) Mg, THF, 25 – 40 °C, 1 h; (b) 2 , 0 – 5 °C, overnight.

All compounds were characterized by ^1H , ^{13}C NMR, and high-resolution mass spectrometry (HRMS). Structure of **5** was also confirmed by the X-ray diffraction method (XRD) (Figure 1A,B). The NMR data of intermediates and title product are presented in the Supplementary Materials.

The bond lengths and bond angles in **5** have typical values for this class of compounds [12] (Figure 1). According to XRD, **5** crystallizes with two independent molecules ($Z' = 2$) in the non-centrosymmetric (chiral) space group $P2_1$. Taking into account that two independent molecules in **5** are characterized by the opposite configuration of the C(1) asymmetric center, we can conclude that **5** is a rather rare example of quasi-racemate [13].

The conformations of two independent molecules (A and B) in **5** are almost identical, thus leading to the presence of the non-crystallographic center of symmetry. The main difference between the two enantiomers in **5** is the slight variation of HO–C–C torsion angles. This variation is the consequence of different roles of OH-groups in the supramolecular organization in **5**. The OH group of one of the independent molecules (A) participate in the formation of OH...OH hydrogen bond (O(1)–H(1O)...O(1A), H(1O)...O(1A) 2.15 Å, OHO 175°, O(1)...O(1A) 2.969(5) Å) with the other molecule (B), while the hydrogen atom of the OH group of the molecule B participates only in the formation of the rather weak and unusual OH...H–C interaction (H...H 2.23 Å, OHH 143°), with the shortest O–H...O intermolecular distance as much as 3.723(5) Å (Figure 1).

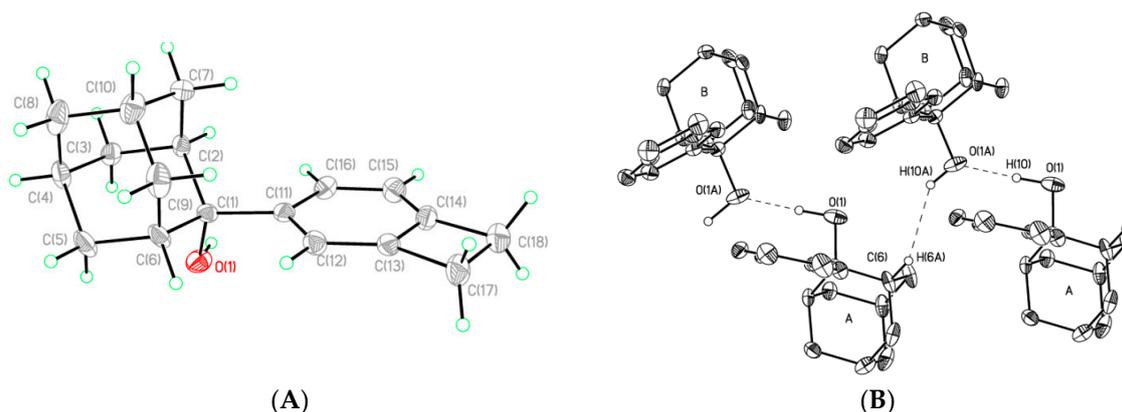


Figure 1. (A) The general view of one of the independent molecules of **5** in representation of atoms by thermal ellipsoids ($p = 50\%$). Selected bond lengths (A): O(1A)–C(1) 1.460(4), C(11)–C(12) 1.405(5), C(11)–C(16) 1.412(5), C(12)–C(13) 1.399(5), C(13)–C(14) 1.386(5), C(14)–C(15) 1.387(5), C(14)–C(17) 1.527(5), C(15)–C(16) 1.382(5), C(15)–C(18) 1.518(5), C(17)–C(18) 1.579(6); (B) OH...O bonded dimers in the crystal of **5**.

3. Materials and Methods

NMR spectra were recorded on a Bruker AM-300 or a Bruker Avance 600 spectrometer (Bruker Corporation, Billerica, MA, USA) in CDCl_3 . Mass spectra were obtained on a Varian MAT CH-6 instrument (Varian, Inc, Palo Alto, CA, USA) using a direct inlet system; the ionization energy was 70 eV; the acceleration voltage was 1.75 kV. The reaction mixtures were analyzed and the purity of all products was checked by TLC on Merck Silica gel 60 F254 UV-254 plates.

2-(Bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-adamantan-2-ol (**5**)

4-Bromobenzocyclobutene (1.22 g, 6.7 mmol) was added dropwise to Mg (160 mg, 6.7 mmol) and a crystal of I_2 in THF (30 mL) under Ar atmosphere at a temperature of 25–40 °C. Magnesium was completely dissolved after 1 h of stirring. Adamantan-2-one (1.0 g, 6.7 mmol) in THF (7 mL) was added to the resulting Grignard reagent and the mixture was stirred overnight. Water (20 mL) was added to the reaction mixture that was then extracted with ethyl acetate (3×20 mL), dried and evaporated. The resulting crude product **5** was purified by flash chromatography to give **5** (1.23 g, 73%) as colorless crystals. **5**: m.p 76–77 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.43 (d, $J = 7.7$ Hz, 1 h), 7.29 (s, 1 h), 7.09 (d, $J = 7.8$ Hz, 1 h), 3.20 (s, 4 h), 2.58 (m, 2 h), 2.43 (m, 2 h), 1.95–1.85 (m, 1 h), 1.85–1.65 (m, 9 h). ^{13}C NMR (75 MHz, CDCl_3) δ 146.0, 144.8, 144.2, 123.9, 122.7, 119.7, 76.0 (COH), 39.2, 37.7, 35.8, 34.9, 33.1, 29.5, 29.4, 27.5, 27.0. HRMS, found ($\text{M}^+ - \text{H}_2\text{O}$): 237.1639, calculated ($\text{M}^+ - \text{H}_2\text{O}$): 237.1639.

Crystals of **5** [$\text{C}_{18}\text{H}_{22}\text{O}$, MW = 254.35] were grown by a slow evaporation of chloroform solution and are monoclinic, space group $P2_1$, at 120(2) K $a = 6.3740(8)$, $b = 19.523(2)$, $c = 11.3239(14)$ Å, $\beta = 104.066(3)$, $V = 1366.9(3)$ Å³, $Z(Z') = 4(2)$, $d_{\text{calc}} = 1.236\text{g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.74\text{ cm}^{-1}$. Intensities of 17,039 reflections were measured with Bruker APEX-II CCD [$\lambda(\text{MoK}\alpha) = 0.71072$ Å, $2\theta < 58^\circ$] and 7273 independent reflections ($R_{\text{int}} = 0.0607$) were used in the further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. C-H hydrogen atoms in **5** were placed in calculated positions and were refined in the “riding” model with $U(\text{H})_{\text{iso}} = 1.2U_{\text{eq}}$ of their parent atoms. The hydrogen atoms of the OH groups were located from the Fourier density synthesis and refined in an isotropic approximation. The refinement converged to $wR_2 = 0.1368$ and *goodness-of-fit* (GOF) = 0.998 for all independent reflections ($R_1 = 0.0605$ was calculated against F for 5073 observed reflections with $I > 2\sigma(I)$). The maximum and minimum values of difference density were 0.262 and -0.253 e \AA^{-3} . All calculations were performed using SHELXTL-2017. Cambridge Crystallographic Data Centre contains the supplementary crystallographic data for this paper No. CCDC 1943491. These data can be obtained

free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

A new 2-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-adamantan-2-ol with a 2-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl) substituent in the 2-position was obtained via a three stage synthesis starting from benzocyclobutene and adamantane. Target product can be useful for the development of new materials with good thermal stability and dielectric properties.

Supplementary Materials: CIF, MOL files, and NMR data of title compound are available online, Figure S1: ^1H NMR of compound 4, 4-Bromobenzocyclobutene; Figure S2: ^1H NMR of compound 2, Adamantan-2-one; Figure S3: ^1H and ^{13}C NMR of compound 5, 2-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)-adamantan-2-ol.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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(28–30 g, 67–71%) 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).

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