



Synthesis and thermal properties of a new styryl-functionalized pentafulvene glassy carbon precursor



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ARTICLE INFO

Article history:

Received 24 March 2014

Received in revised form 28 May 2014

Accepted 29 May 2014

Available online 4 June 2014

Keywords:

Fulvene

Carbon precursor

Crosslinking

Styrene

Glassy carbon

ABSTRACT

The first preparation of a styryl-functionalized aryl pentafulvene **4** was carried out. In the crystal structure of **4**, the packing of fulvene molecules results in the shortest intermolecular contacts between aligned vinyl groups. Thermal reactivity studies of **4** (DSC and TGA, under N₂) revealed a small difference between the melting point (120 °C) and the T_{onset} for cross-linking (125 °C), and provided strong evidence for the production of a network material (**net4**) due to reactivity of the attached styryl group. Pyrolysis of **net4** under N₂ gave a glassy carbon product in low yield as revealed by powder X-ray and TGA analyses (carbon yield (TGA) of 38% (900 °C)).

Published by Elsevier Ltd.

1. Introduction

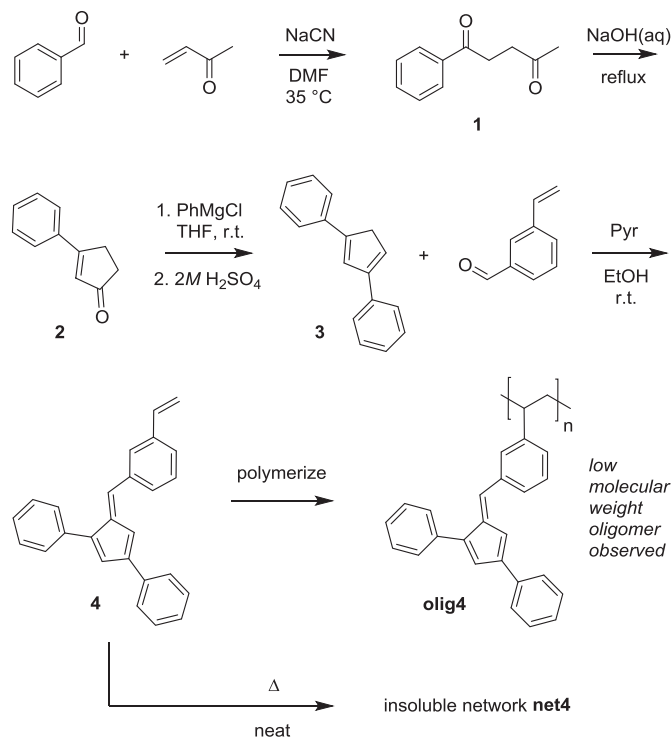
The ability to specifically tailor structure to achieve a desired property is a goal of central importance in organic materials chemistry. For this reason, the pentafulvene molecular architecture has received significant research attention due to possibilities for structural and functional variability around a central conjugated system. Synthetic strategies that employ electron rich or deficient substituents in addition to substituents that control stereochemistry or influence structure or reaction chemistry have been used to design novel fulvene derivatives with desired optical, electronic, structural, and reaction properties. This has led to a growing array of applications for various pentafulvene systems including metal-locene^{1–3} and supramolecular chemistry,⁴ organic light emitting diodes (OLEDs),⁵ additives for solar cells,^{6,7} donor- π -acceptor 'push-pull' systems,⁸ and thermally stable and soluble chromophores.⁹ An intriguing application, and one that has not been widely investigated, is the conversion of appropriately substituted pentafulvenes to glassy carbon materials.

Glassy carbon (also called vitreous carbon) is a non-crystalline form of carbon that cannot be converted to the graphite form even at high temperatures (>3000 °C).¹⁰ The structure of glassy carbon remains unknown, although several models have been suggested including one in which fullerene like curved sheets,

consisting of 5, 6, and 7 membered rings are involved.¹¹ Synthetic methods for glassy carbon involve crosslinking of high carbon content, small molecules, and subsequent carbonization at temperatures close to 1000 °C. As an example, bis-*ortho*-diynylarene (BODA) monomers, undergo Bergman cyclopolymerizations^{12,13} to form hyper-branched, rigid naphthalene networks that can be further carbonized at 1000 °C to form glassy carbon in high yield.¹⁴ Resistance to harsh chemical and thermal conditions as well as low gas permeability, structural stability, and other electronic properties have made glassy carbon attractive for refractory applications and for the miniaturization of microelectronic components. For example, BODA-derived glassy carbon has shown utility for thin film dielectrics,¹⁴ photonic materials,¹⁵ and as precursors for carbon fibers^{15,16} and micrometer scale structures.^{16–18} The ongoing efforts to miniaturize and improve microelectronic device fabrication and performance will benefit from studies directed towards the synthesis of inexpensive, melt processable precursors that cross-link to form glassy carbon materials.

In this paper, we report a preliminary study of fulvene derived glassy carbon precursors with a study of the synthesis and thermal chemistry of the styryl-functionalized aryl fulvene (**4**) (Scheme 1). Fulvene **4** undergoes concurrent melt transition and facile thermal cross-linking steps to afford a glassy carbon material. Although phenyl substituted pentafulvenes have been investigated as glass forming materials,^{19,20} thermal crosslinking studies of pentafulvenes via reactive functional groups to form network materials that can be subsequently converted to glassy carbon have not been carried out.

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Scheme 1. Synthesis of styryl-functionalized fulvene **4** and preparation of its oligomer **olig4** and network **net4**.

2. Results and discussion

2.1. Synthesis of 1,3-diphenyl-6-(3-vinylphenyl)fulvene **4**

1,3-Diphenyl-6-(3-vinylphenyl)fulvene **4** was obtained in multi-gram quantities using an overall four-step reaction sequence as outlined in Scheme 1. This method was recently employed for the preparation of a pool of 6-aryl/alkyl-substituted fulvene chromophores.⁹ Pentanedione (**1**) was obtained via Stetter coupling of benzaldehyde with methyl vinyl ketone. The cyclization of **1** to 3-phenyl-cyclopenten-1-one (**2**) was conveniently executed via base-promoted intramolecular aldol condensation. Installation of the phenyl group was achieved via Grignard reaction of **2** with PhMgCl to afford 1,3-diphenyl-1,3-cyclopentadiene (**3**). The conditions of Little and Stone²¹ were used to synthesize the key styryl-functionalized fulvene **4** from 2-vinylbenzaldehyde and **3** in 66% isolated yield. Purity and structure were confirmed by melting point, GC/MS, and NMR (¹H, ¹³C). Single crystal X-ray analysis confirmed the molecular structure of **4** as well as revealing vinyl groups positioned with the shortest intermolecular contacts.

2.2. X-ray analysis of 1,3-diphenyl-6-(3-vinylphenyl)fulvene **4**

Fulvene **4** crystallized out in the centrosymmetric space group, C2/c, with one molecule per asymmetric unit. In the molecular structure of **4** (Fig. 1) alternating long and short ring C–C distances as well as the intra-ring angles are all consistent with the basic pentafulvene structure and with the structures of other 6-alkyl/aryl substituted 1,3-diphenylfulvenes reported recently (Table 1).⁹ To our knowledge, there are no published structures of pentafulvenes with attached styryl units. Therefore, an analysis of the vinyl group parameters of **4** were made in reference to the reported data for styrene,²² 4-vinylbenzoic acid,²³ and 9-vinylanthracene.²³ The vinylic C–C bond distance of **4** is comparable to all three of these compounds, and has a torsion angle from the Ph group closest to the corresponding torsion angles adopted for styrene and 4-

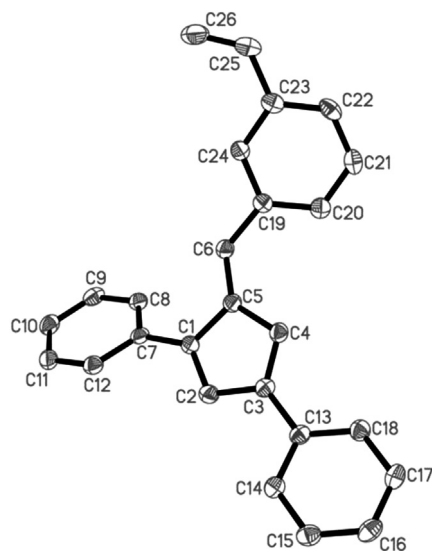


Fig. 1. Thermal ellipsoid view of fulvene **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

Table 1
Selected bond distances and angles

Ring bond distances (Å)					
Fulvene ^a	C1–C2	C2–C3	C3–C4	C4–C5	C5–C6
4	1.357(2)	1.469(2)	1.360(2)	1.462(2)	1.353(2)
6-Ph	1.355(2)	1.466(2)	1.360(2)	1.460(2)	1.354(2)
6-py	1.353(2)	1.467(2)	1.363(2)	1.459(2)	1.357(2)
Substituent angles (°) ^b					
Fulvene ^a	1-Ph	3-Ph	6-R		
4	37.27(7)	21.26(9)	31.28(9)		
6-Ph	28.12(6)	20.38(7)	44.60(5)		
6-py	42.11(6)	22.80(8)	50.51(4)		
Comparison of vinyl group parameters					
Compound ^c	Vinylic C–C (Å)	Torsion angle versus ring ^d			
4	1.320(3)	9.1(3)			
Styrene (83 K)	1.3245(16)	7.82(17)			
4-Vinylbenzoic acid (108 K)	1.3248(14)	9.06(16)			
9-Vinylanthracene (123 K)	1.3266(15)	56.14(14)			

^a Symbols, 6-Ph and 6-py, refer to 6-phenyl-(exocyclic *E*-isomer) and 6-(1-pyrenyl)-1,3-diphenylfulvenes, respectively. Data were obtained from Ref. 9.

^b Angle between the least squares plane of the tabulated substituent with respect to the least squares plane defined by C1–C5.

^c Data for styrene, 4-vinylbenzoic acid, and 9-vinylanthracene were obtained from Refs. 22,23.

^d Torsion angle C24–C23–C25–C26.

vinylbenzoic acid (Table 1). Comparison of substituent angles of **4** versus structurally related 1,3-diphenyl-6-phenylfulvene and 1,3-diphenyl-6-(1-pyrenyl)fulvene (Table 1) shows some notable differences, especially between the 6-R angle of **4** versus the 6-Ph fulvene, and is a reflection of differences in crystal packing enforced by the vinyl group of **4**.

Molecules of **4** pack in layers running parallel to the *c*-direction and in a bilayer sequence along the *a*-direction (Fig. 2). This forms interleaving T–T (tail (T)=1,3-diphenylfulvene rings) and H–H (head (H)=3-vinylphenyl rings) associations that alternate along the *a*-direction, similar to those observed in the crystal structure of 1,3-diphenyl-6-(1-pyrenyl)fulvene.⁹ The side by side arrangement of molecules along the *c*-direction is such that the planes of the fulvene rings (mean plane defined by C1–C5) are tilted by 46.1° in alternating directions with respect to the 010 plane, and are

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