

Synthesis and characterisation of *N*-substituted bis-phenols as precursors for unsymmetrical triarylmethane cations

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Abstract

Bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane derivatives (**1–6**) are synthesised and characterised. Inclusion of acetonitrile by bis-(4-hydroxy-3,5-dimethylphenyl)(4-*N,N'*-dimethylaminophenyl)methane is observed in the crystal structure. Cations generated from these compounds have characteristic visible absorptions. An alternative method for generation of these cations from quinone methide namely 4-[(4'-hydroxy-3',5'-dimethylphenyl)(4-*N,N'*-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone under very mild condition is described. The characteristic absorption peaks of the cationic species are used to distinguish different isomeric forms.

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1. Introduction

The triarylmethane cations are relatively easy to generate and are stable [1–7]. These cations are generally prepared from the triphenylmethanes by using superacids [5–7]. Isomeric forms of a triarylmethyl cation can be proposed depending on the substituents present on the rings [8,9]. A phenyl substituted bis-phenol would provide precursors for generation of isomeric cations and complexity of such cations will be enhanced with incorporation of multiple units [10–12]. In the present investigation we have carried out spectroscopic study on bis-phenols which have substituted or unsubstituted aminophenyl units as well as phenolic groups. The presence of a nitrogen atom in one of the aromatic ring of these compounds would provide scope for the isomeric cations. With the objectives to differentiate such cations in solution we have synthesised several bis-phenolic

compounds whose characterisation and properties of the cationic species are discussed.

2. Results and discussion

The nitrogen-containing bis-phenols **1–4** are synthesised and characterised (Fig. 1). The bis-phenol **1** is prepared from the bis-(4-hydroxy-3,5-dimethylphenyl)(4-nitrophenyl)methane. Reduction of the nitro group with $\text{NH}_2\text{NH}_2\text{-Pd/C}$ gave the corresponding amino derivative namely bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane. Compounds **3–4** are synthesised by derivatising **1**. The bis-(4-hydroxy-3,5-dimethylphenyl)(4-*N,N'*-dimethylaminophenyl)methane **2** is synthesised by acid catalysed condensation of 2,6-dimethylphenol with 4-*N,N'*-dimethylaminobenzaldehyde. In general bis-phenolic compounds possess extensive H-bonded structure and these compounds are no exception to this. For example, in solution **2** has extensive H-bonding with solvents and is clearly reflected in the $^1\text{H NMR}$ spectra recorded in different solvents. The compound **2** has characteristic A_2B_2 pattern from the aromatic ring

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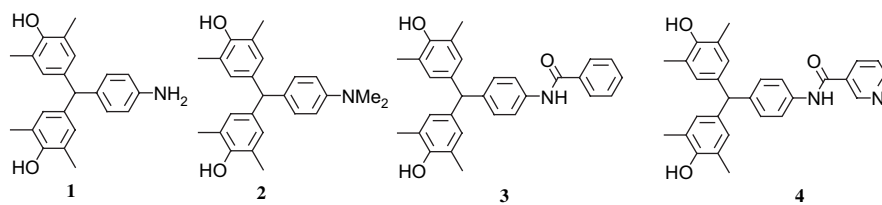


Fig. 1.

containing dimethylamine group and it has also signals arising from proton on the ring at *meta* to the hydroxyl groups. This signal is very sensitive to the solvent. In methanol- d_4 this signal appears at 6.58 ppm, whereas in acetonitrile- d_4 it appears at 6.69 ppm. The ^1H NMR spectrum of the compound **2** in a mixture of two solvents ($\text{CD}_3\text{OD} + \text{CD}_3\text{CN}$) shows that this peak appears at 6.67 ppm. Thus, protic solvents interact with the $-\text{OH}$ group of the bis-phenol causing shifts in the ^1H NMR signals of the ring protons. The effect of hydrogen bonding with solvent molecules is reflected in solid-state structure of the compound also. The compound **2** was crystallised from acetonitrile as 1:1 adduct with the solvent. In the crystal structure it is clear that **2** has a propeller-like conformation (Fig. 2) and the molecules are held together through $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interaction along crystallographic *c*-axis. The acetonitrile molecules are held in between two bis-phenolic units and the $\text{C}\equiv\text{N}$ of the acetonitrile unit is coordinated to one the phenolic $-\text{OH}$ group. Interestingly the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the phenolic OH -groups in the molecules of **2** are not disrupted by the interaction with the acetonitrile. The arrangement of the acetonitrile in the crystal lattice has very organized features. Looking at the perpendicular view on the longitudinal arrangement of acetonitrile it is very clear that the alternative molecules are arranged in same disposition. But the acetonitrile next to each other has very projection such that if the $-\text{C}\equiv\text{N}$ unit is projecting

upward in one case the next $-\text{C}\equiv\text{N}$ unit is projected downward.

The di-bis-phenols (**5–6**) are synthesised by functionalisation of bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane **1** (Scheme 1). The parent bis-phenol **1** is linked with amide linker by treating it with acid chloride of the corresponding dicarboxylic acid (Scheme 1). The important feature of the two molecules **5** and **6** is that the bis-phenol units are separated by a rigid amide spacer. These two molecules in solution do not self-assemble and is confirmed by mass spectroscopy.

A triarylmethane cation may be symmetric or non-symmetric based on the nature of the aryl units anchored to the central carbon atom. To look at such possibilities arising from the presence of a nitrogen-containing functional group; four monomeric substrates **1–4** were treated with trifluoroacetic acid to generate their corresponding cations. Formation of the cation from **2** is relatively easy, compared to either **3** or **4**. However, the same cation of **2** can be alternatively generated by treatment of the quinone methide, namely 4-[(4'-hydroxy-3',5'-dimethylphenyl)(4-*N,N'*-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone with mineral acid, the quinone methide in turn can be prepared by oxidation of the corresponding bis-phenol **2** by ammonium persulphate. The generation of cation from the quinone methide involves protonation of the quinone methide with a mineral acid, as shown in Scheme 2 for **7**. Similar cation

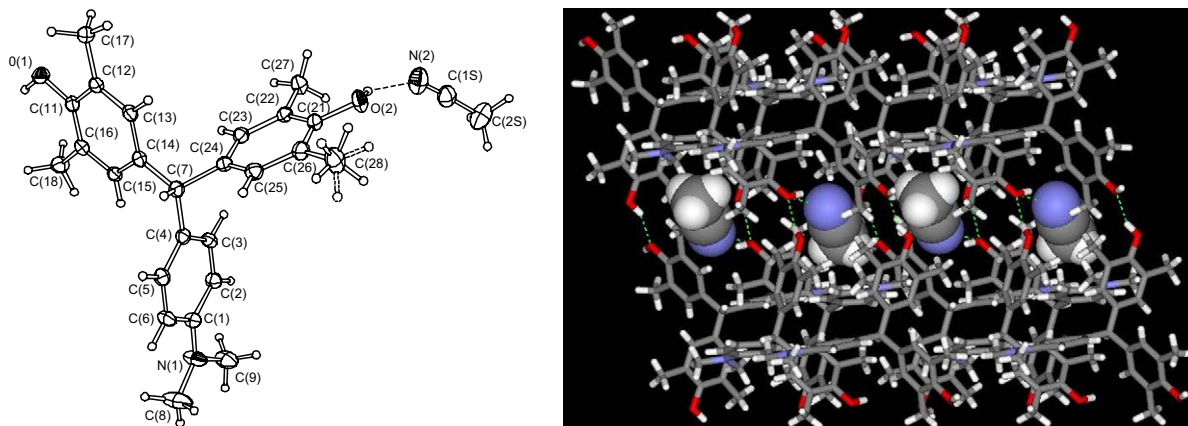


Fig. 2. Crystal structure of 1:1 adduct of **2** with acetonitrile and the packing of the solvent molecules in the crystal lattice showing the hydrogen-bonding interactions [monoclinic, $\text{P}2(1)/c$; *a*, 12.146(3); *b*, 15.584(4); *c*, 13.294(3); β , 107.61(1); selected bond distances (Å) and bond angles ($^\circ$): $\text{N}2-\text{C}1\text{S}$ 1.140(3); $\text{N}2-\text{C}1\text{S}\cdots\text{C}2\text{S}$ 178.5(2); $\text{O}2-\text{H}02\cdots\text{N}2$ 2.845(2) 147(2); $\text{O}1-\text{H}01\cdots\text{O}2$ 2.751(17) 150(2); $\text{O}1-\text{H}01$ 0.89(3); $\text{N}1-\text{C}1$ 1.384(2); $\text{O}2-\text{H}02$ 0.92(3); $\text{N}1-\text{C}1$ 1.384(2); $\text{C}1-\text{N}1\cdots\text{C}8$ 119.03 (15); $\text{C}1-\text{N}1\cdots\text{C}9$ 119.16 (14); $\text{C}8-\text{N}1\cdots\text{C}9$ 118.75 (15)].

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