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Weak interactions direct crystal packings of arylated 1,3-butadienes

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HIGHLIGHTS

- Four novel arylated 1,3-butadienes were prepared.
- Isomers in solution were studied by NMR and UV/Vis spectroscopy.
- Crystal packing of the compounds is directed by weak interactions, only.

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ABSTRACT

Four novel aryl butadienes (substituted with R = Cl, OCH_3, NO_2 and H) were prepared and characterised by X-ray diffraction, IR, UV/Vis and NMR spectroscopies. A comparative analysis of crystal packings was aimed to determining influence of weak interactions: C—H···O and C—H···Cl hydrogen bonds, C—H···π interactions and dispersion interactions. Since no proton donors is present and since the molecules are sterically very similar, these weak interactions are responsible for wide variation in 3D packing and supramolecular motives.

1. Introduction

Crystal engineering using strong, directional intermolecular interactions such as hydrogen bonds, dipolar interactions and agostic interactions is very well-known [1–4]. Common supramolecular motives, called 'supramolecular synthons' and 'tectons', have been recognised, and can be quite reliably used in design of molecular crystals [5–8]. However, crystal packing of organic compounds lacking strong proton donors and acceptors is less studied [9,10]. Such compounds are capable of forming only weak interactions, which rarely, if ever, form commonly recognisable motives. Therefore, a study of a series of closely related compounds lacking proton donors and acceptors could be useful to find out factors influencing their crystal packing. As a model system, we chose several aryl substituted butadiene derivatives (compounds **1**–**4**, Scheme 1).

1,3-Butadienes and their derivatives represent a class of well-studied compounds. The interest in this kind of compounds has spread from manufacture of synthetic rubber, latex paints, and nylon to modern drug design [11]. Under prolonged conjugated system these derivatives also show a versatile photoreactivity and formations of various photoproducts with remarkable electrochemical, optical, physical and biological properties [12–15]. Their skeleton has also proved to be useful reactive intermediate in various stereoselective transformations making these derivatives powerful building blocks in organic synthesis [16–19].

In continuation of our interest on intra- and intermolecular photocycloaddition reactions of 1,3-butadiene derivatives, molecule that combine the properties of both butadiene and hexatriene systems [11–14], we extended synthesis to new aryl butadienes **1**–**4** (substituted with R = H, Cl, OCH_3 and NO_2). In these compounds, the butadiene groups in the position 1, 2, 3 and 4 are not equivalent and might behave quite differently in the primary process of photoisomerization. It was interesting to distinguish the ethylenic moieties of the butadiene groups in the position 1, 2, 3 and 4 to be able to follow the path of the primary photoreaction. Therefore, molecules of very similar structures can show dramatically different photoinduced behaviour producing various photoproducts intersting for further functionalization using simple aproach with light as reagent.

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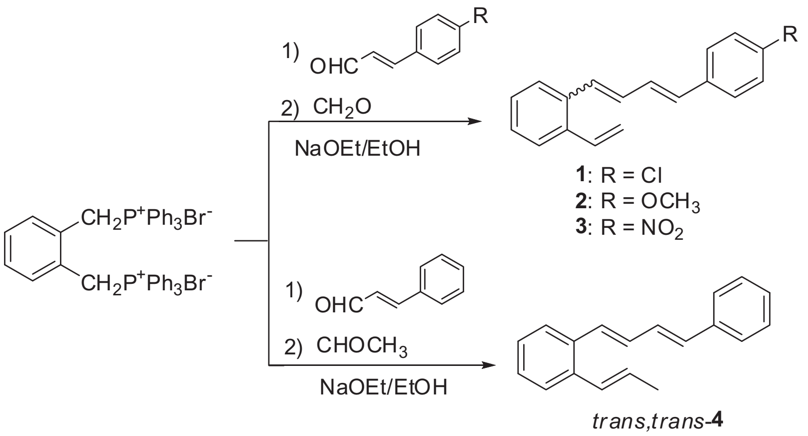

Scheme 1. Synthesis of butadiene derivatives **1**–**4** by Wittig reaction.

2. Results and discussion

2.1. Synthesis and spectroscopic characterisation

Butadiene derivatives **1**–**4** were prepared by Wittig reaction from diphosphonium salt and the corresponding cinnamaldehydes (Scheme 1). The products were obtained in good yields (65–78%) as mixture of *cis*- and *trans*-isomers, which were separated by column chromatography and completely characterised spectroscopically. The syntheses were performed always from the corresponding (*E*)-geometric isomers of the cinnamaldehyde, where the second double bond (looking from the *ortho*-substitued central benzene ring) in the products retain the (*E*)-configuration. Hence, the number of geometric isomers was reduced.

Fig. 1 display the normalised absorption spectra of *trans*-isomers of **1**–**4** in ethanol. Band absorption maxima of all derivatives are found in the range of 325–380 nm, and clearly show substituent influence on absorption characteristic. Chloro and methoxy derivatives **1**–**2** show a slight bathochromic shift (15–20 nm) compared to the unsubstitued derivative **4**. Nitro derivatives **3** results in significant bathochromic shift (55 nm), compared to the absorption bands of the previous componds **1**, **2** and **4**. This effect may be a consequence of the more than doubled dipole moment of the nitro derivatives in the excited state.

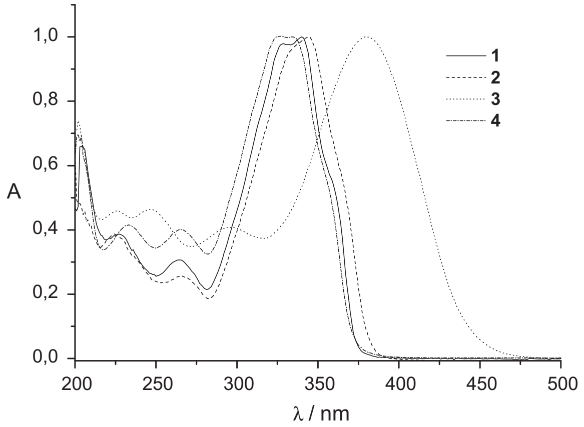

Fig. 1. Normalised absorption spectra of **1**–**4** in ethanol.

The ^{1}H NMR spectra of the studied compounds **1**–**3** with the emphasis on ethylenic protons are presented in Fig. 2. The ethylenic protons in all examples appear between 6.61 and 7.13 ppm as doublet (H_A, H_D protons) or doublet of doublets (H_B, H_C protons). The signals of H_D protons are shifted to higher field (6.61–6.70 ppm) in comparison to the H_A protons (6.91–7.11). Signals of H_B and H_C protons are widespread between 6.80–7.13 ppm. The signals in all examples **1**–**3** are very similar and have

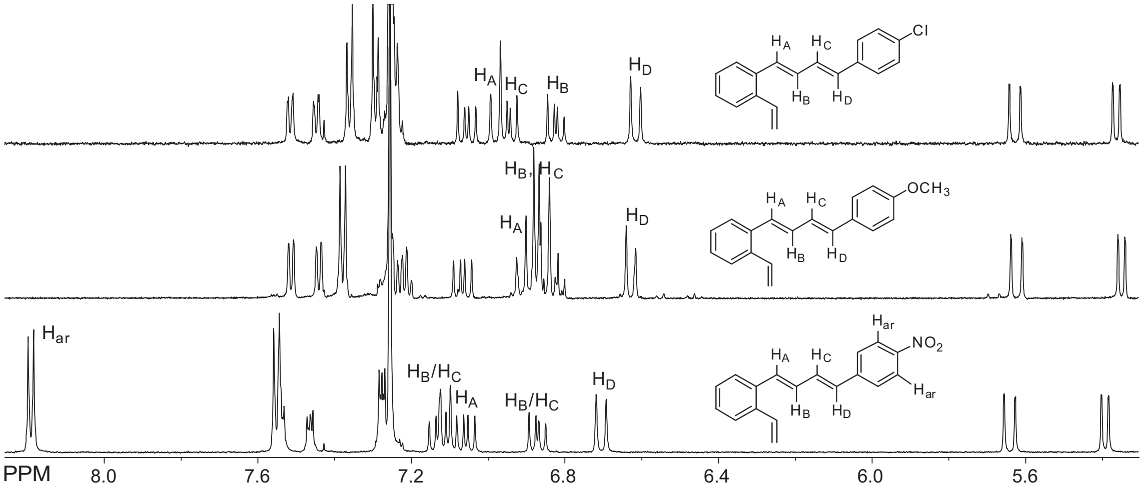

Fig. 2. ^{1}H NMR spectra ($CDCl_3$, 600 MHz) of **1**–**3**.