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Novel arylated chloro- and methoxy-1,3-dibutadienes: Influence of substituents on molecular conformation and crystal packing

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HIGHLIGHTS

- Three novel arylated 1,3-butadienes were prepared.
- Isomers in solution were studied by NMR and UV/Vis spectroscopy.
- Influence of the substituents (and different positions of substituents) on the molecular conformation.

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ABSTRACT

Three novel arylated chloro- and methoxy-1,3-butadienes were prepared and studied by a combination of spectroscopic (UV/vis, IR and NMR) and X-ray crystallographic methods. Influence of substituent on the molecular conformation and crystal packing (i.e. intermolecular interactions) was studied. It was predicted that the differences in electronic and steric effects of two chlorine atoms in comparison to two methoxy groups as substituents at different locations in the molecule would provide various packing of the molecules and cause different assumptions for the photochemical behaviour.

Introduction

Synthetic organic photochemistry occasionally provides an easy access to complicated structures, difficult to obtain by a classical synthetic approach [1]. Among the most studied and used reactions are the intra- and intermolecular photocycloadditions [2]. Important precursors for these reactions are butadiene derivatives of *o*-divinylbenzenes. Under their prolonged conjugated system, these compounds could participate in photochemical reactions and give novel complex structures [3,4].

In order to study the influence of chlorine as a substituent on the photochemical behaviour of conjugated butadiene systems [5–7], dichloro derivatives of butadiene **1**–**2** were synthesized. The initial compounds **1**–**2** undergo photochemical reaction to give new polycyclic structures [4]. Their formation depends on the electronic and steric effects of two chlorine atoms, bounded as substituent on different locations in the molecule. Chlorine can affect on dibutadiene unit by mesomeric and inductive effect. Understanding the key effects of chlorine substituent in photochemical reaction of these butadiene derivatives, makes the synthesis of these systems suitable for routing photoreaction towards various interesting structures for further transformations and functionalization.

In continuation of our interest in effect of substituent on intramolecular photocycloaddition reactions, we extended synthesis to para-metoxy substitued 1,3-butadiene derivative **3**. It could be expected that very similar compounds with different substitution may display diverse photoreactivity and consequently new type of products, interesting for further studies.

Results and discussion

Synthesis and spectroscopic characterization

Butadiene derivatives **1**–**3** were prepared by Wittig reaction from diphosphonium salt and the corresponding cinnamaldehydes (Scheme 1). The products were obtained in good yields (50–70%)

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as mixture of three isomers (*cis,cis*-, *cis,trans*- and *trans,trans*-), which were separated by column chromatography and completely characterised spectroscopically. Because the synthesis were performed always from the corresponding (*E*) geometric isomers of the cinnamaldehyde, the second double bond (looking from the *ortho*-substitued central benzene ring) in the products retain the (*E*) configuration. Hence, the number of the geometric isomers was reduced.

Fig. 1a shows the absorbtion spectra of starting *trans,trans*-isomers **1**–**2** in ethanol. Band absorption maxima of these compounds are found in the range of 350–375 nm. *Trans,trans*-isomer of **2**, which has the same configuration but different location of chlorine atoms substitution, show a bathochromic shift in comparison to *trans,trans*-isomer of **1**. This effect can be explained by better delocalization of π-electrons in the absence of the chlorine on the butadiene units.

The UV spectra of separated *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of metoxy derivative **3** clearly show the configuration influence on absorption characteristic (Fig. 1b). Maxima wavelengths of these isomers are in the range of 300–400 nm. The *trans,trans*-isomer show a bathochromic shift and an increase of the molar absorption coefficient in comparison to their *cis,trans*- and *cis,cis*-isomers, as expected. The reason for this effect is increased molecular planarity of *trans,trans* configuration and the possibility of better delocalisation of π electrons.

The ^{1}H NMR spectra of the compounds **1**–**2** are presented in Fig. 2. The signals of ethenylic protons (exept H_B protons of *trans,trans*-**2**) of both derivatives are widespread between 6.60–7.10 ppm, and have very similar chemical shift. Therefore, the effect of position of chlorine atoms is in this case negligible. The exception is H_B ethenylic proton of *trans,trans*-isomer of **2**, which is drastically shifted to 7.44 ppm. The reason for this phenomenon is strong electronic effect of chlorine atoms on butadiene units to nearby protons.

Fig. 3 shows the ^{1}H NMR spectra of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of metoxy derivative **3** with the emphasis on ethylenic protons. These protons in all examples appear as doublet or doublet of doublets between 6.42 and 7.00 ppm. Under increased molecular planarity of *trans,trans*-isomer, the *trans*-ethylenic protons as expected are shifted to higher field, in comparison to the signals of *cis*-protons.

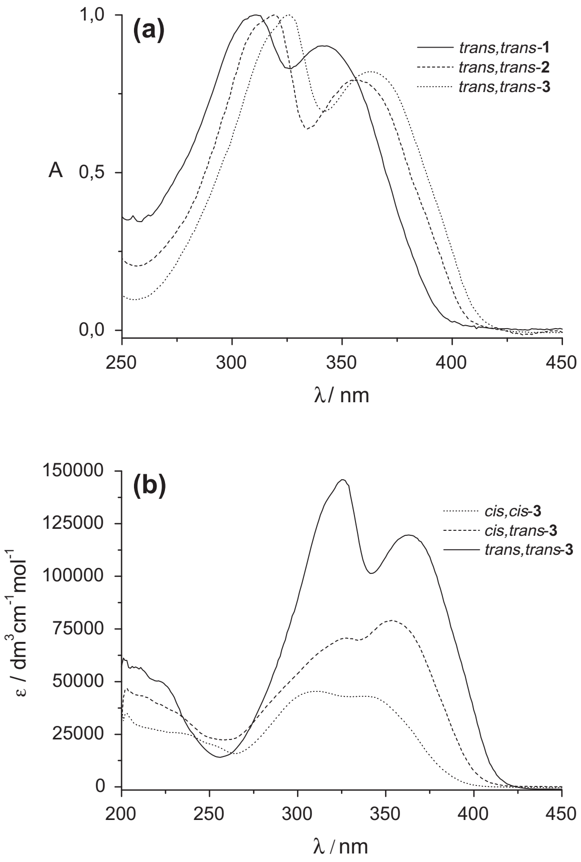
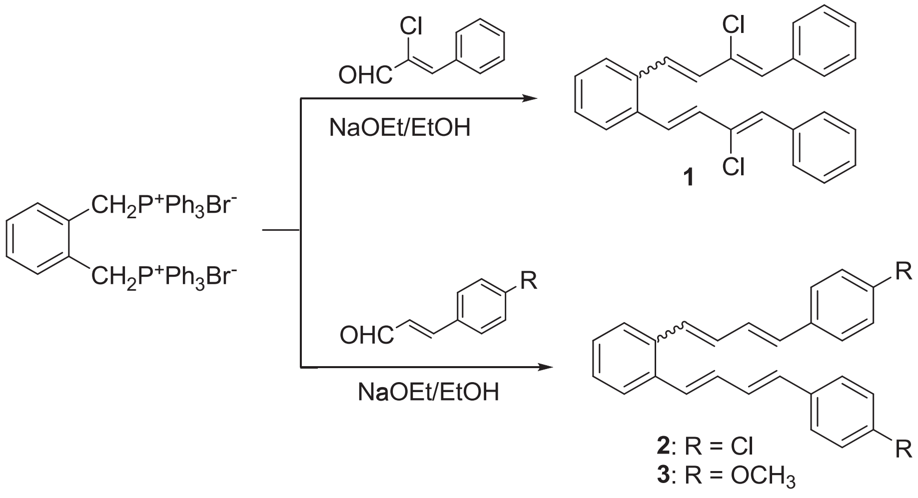


Fig. 1. UV spectra in ethanol: (a) *trans,trans* izomers of compounds **1–3**; (b) *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of compound **3**.

Crystal structures

Conformations of molecules of *trans,trans*-**1** and *trans,trans*-**2** are very different. Symmetry of *trans,trans*-**2** is *Cs* (Fig. 4a), with the crystallographic mirror plane passing through the middle of the central phenyl ring (i.e. bonds C11—C11^i and C13—C13^i, $i = x, y, 1 - z$). The molecule is relatively flat (Fig. 6a), with angle between terminal phenyl groups (C1 → C6) of 28.8°. Molecule of *trans,trans*-**1** is twisted and chiral (Figs. 4b and 5b), its molecular symmetry being C_1. One of its chlorine atoms is disordered over two positions (designated as Cl2 and Cl2a) with respective populations of 0.63 and 0.37.

The entire molecule of each compound comprises a conjugated system, so both can be regarded as single, delocalised, π electron systems. The formally single C—C bonds in the butadienyl fragment (bonds C4—C7, C8—C9 and C10—C11; in *trans,trans*-**1** there are also



Scheme 1. Synthesis of butadiene derivatives **1**–**3** by Wittig reaction.