Journal of Molecular Structure 1051 (2013) 1–14

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and photochemical transformations of new butadiene chromophores: The influence of the nature and position of chlorine substituent on the photoinduced behaviour

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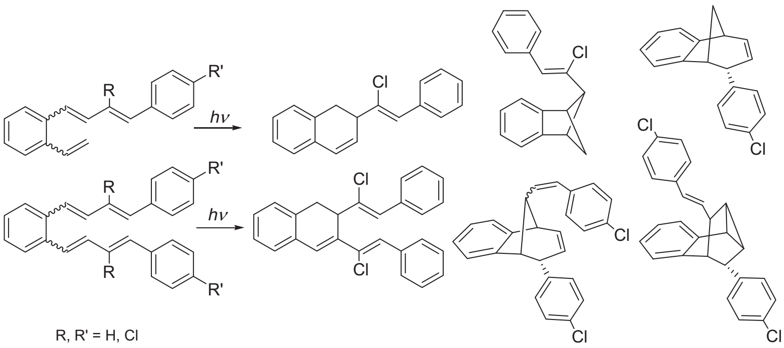
HIGHLIGHTS

- Initial mono- and dichloro-substituted butadienes display diverse photobehaviour.
- α-Chloro derivatives react in the sense of electrocyclization reaction.
- *p*-Chloro-substituted butadienes undergo intramolecular photocycloaddition.
- Competitive effects of chlorine substituents on the photoinduced behaviour.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 12 July 2013
Accepted 22 July 2013
Available online 2 August 2013

Keywords:
Butadiene
Chlorine
Photochemistry
Reaction mechanism
Spectroscopy

ABSTRACT

The photochemical behaviour of mono- and dichloro-substituted butadiene derivatives was studied at low concentrations. These compounds display diverse photochemical behaviour. The α-chloro derivatives photocyclize to give six-membered ring photoproducts. *p*-Chloro-substituted butadienes undergo intramolecular [2 + 2] cycloaddition followed by formation of benzobicyclic structures. The steric hindrance of chlorine(s) in α-position(s) cause a greater deviation from planarity, relative to *p*-substitution, and shift conformer equilibria and affects the reaction pathways and yields.

1. Introduction

Previous publications [1–8] on the photochemistry of different heteroaryl substituted hexatrienes showed interesting intramolecular cycloaddition reactions and the formation of bicyclo[3.2.1]octadienes as unsaturated structural analogues of the bicyclo[3.2.1]octane skeleton which is found in numerous biologically important active natural products [9–12]. By insertion of an additional double bond into the molecule of *o*-vinylstilbene, we obtained the extended conjugated system of *o*-vinyl-1,4-diphenyl-1,3-butadiene **1** (Fig. 1) which might allow the formation of a new polycyclic structure with an double bond functionality for further transformation. The photochemistry of conjugated butadiene

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http://dx.doi.org/10.1016/j.molstruc.2013.07.052

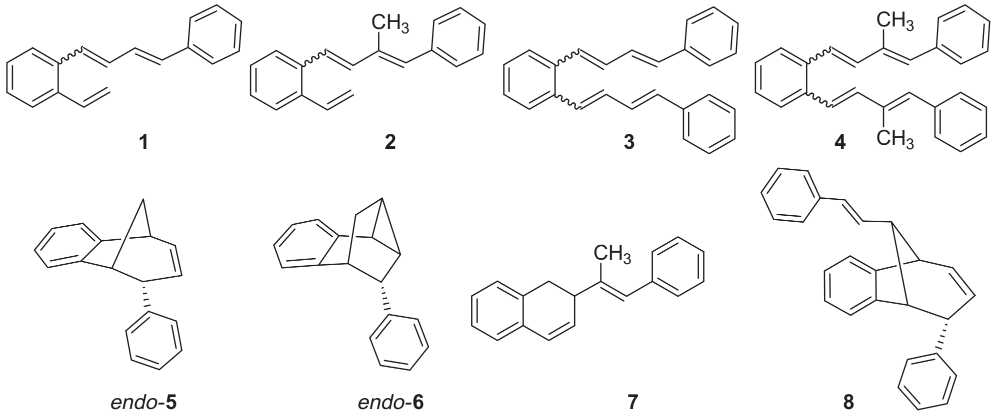
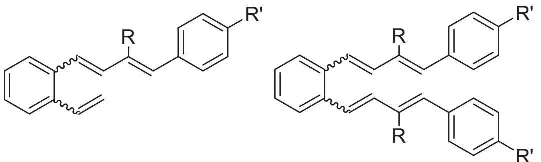


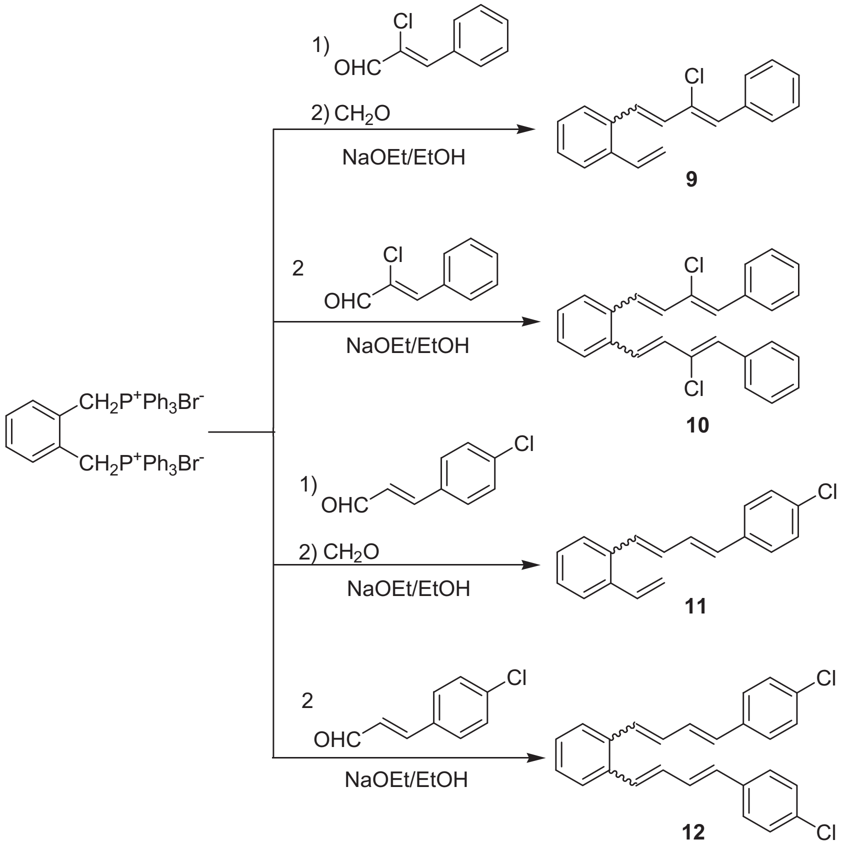
Fig. 1. Structures of the known butadiene derivatives (**1**–**4**) and their photoproducts (**5**–**8**).



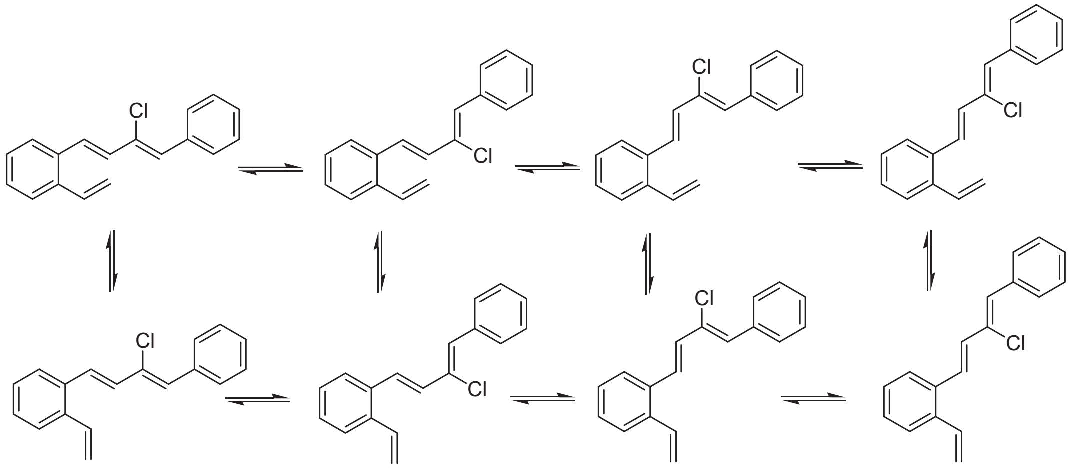
9/**10**: R = Cl, R' = H; **11**/**12**: R = H, R' = Cl

Fig. 2. Structures of the new butadiene derivatives (**9**–**12**).

derivatives **1**–**4** (Fig. 1), molecules that combine the properties of both butadiene and hexatriene systems, has been examined for the first time by our group [13,14]. The unsubstituted compound 1-(*o*-vinylphenyl)-4-phenyl-1,3-butadiene (**1**) undergoes intramolecular photocycloaddition at 350 nm and only the *endo*-phenyl-benzobicyclo[3.2.1]octadiene isomer (*endo*-**5**) was isolated in very good yield (90%) due to the stereoselectivity of the photoreaction. The photoproduct *endo*-**5** underwent further di-π-methane rearrangement at 300 nm leading to a tricyclic structure (*endo*-**6**). The related substituted methyl derivative, 2-methyl-1-(*o*-vinylphenyl)-4-phenylbutadiene butadiene (**2**), on the other hand, rearranges to dihydronaphthalene derivative **7** upon photoirradiation. The effect of the methyl substituents is even more dramatic for dibutadienes **3** and **4**. The parent unsubstituted compound **3** undergoes stereoselective photoinduced intramolecular cycloaddition giving benzobicyclo[3.2.1]octadiene **8**, whereas the



Scheme 1. Structures of the new butadiene derivatives (**9**–**12**).



Scheme 2. Possible conformations of *trans*-isomer of compound **9**.

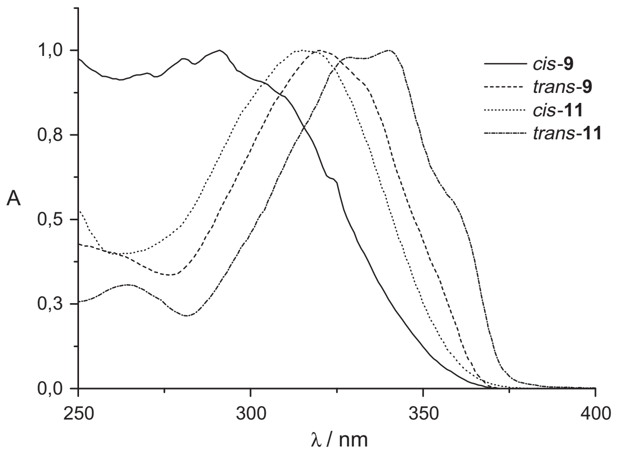


Fig. 3. Absorption spectra of the isomers of compounds **9** and **11** in *n*-hexane.

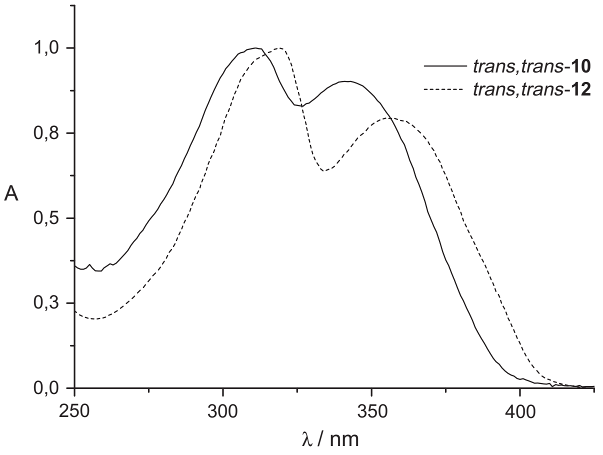


Fig. 4. Absorption spectra of the isomers of compounds **10** and **12** in *n*-hexane.

dimethylated derivative shows only geometrical isomerization due to the steric effect of the substituents. Methyl groups on the butadiene backbones reduce the extent of conjugation, causing a blue-shift of the characteristic absorption band. Furthermore, the fluorescence efficiency is dramatically decreased, as a consequence of nonplanarity and reduced rigidity of the molecules due to the crowding by the methyl and phenyl groups. Thus, four molecules with very similar structures showed dramatically different photoinduced behaviour and emphasize that changes of the nature and position of the substituents are essential in understanding the photochemistry of these types of compounds.

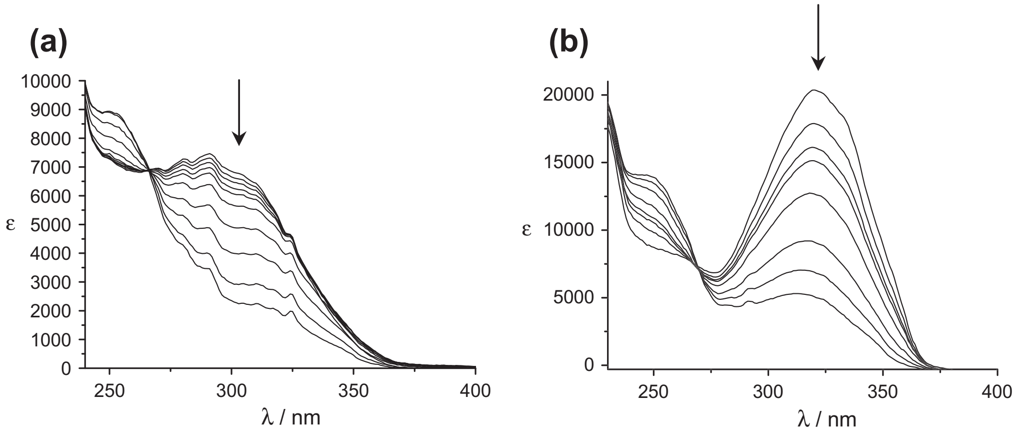


Fig. 5. Spectral change during the irradiation of *cis*-**9** in *n*-hexane (a) after 0, 1, 2, 4, 8, 16, 32, 64, 128, 256 and 512 s and *trans*-**9** in *n*-hexane (b) after 0, 1, 2, 4, 8, 16, 32, 64 s (λ_{ir} = 350 nm, ℓ = 1 cm).

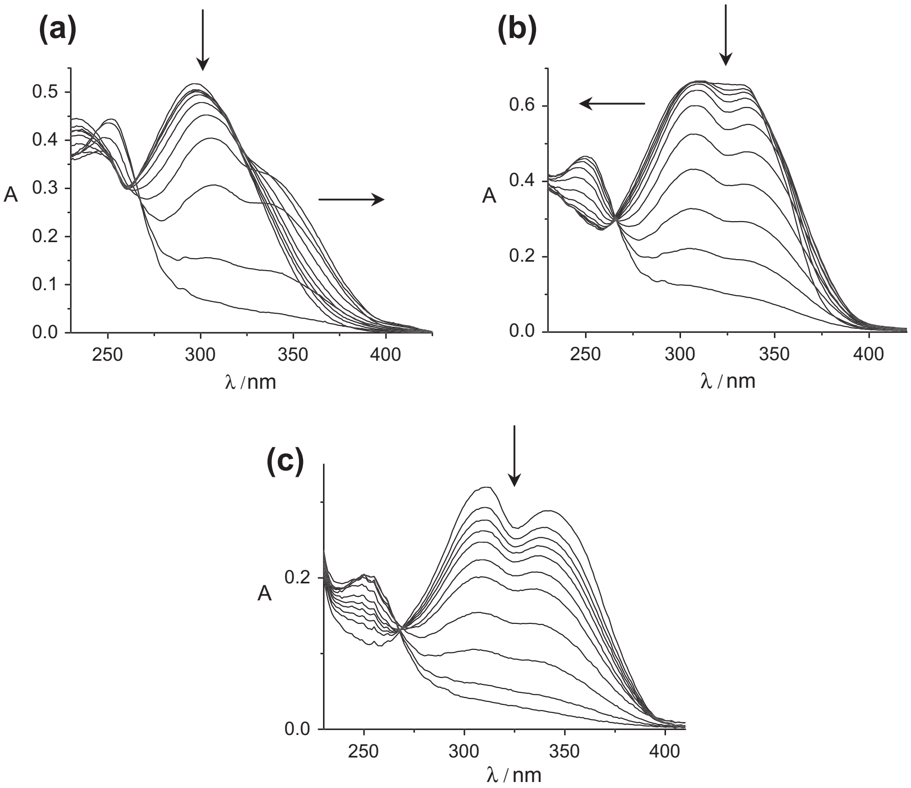


Fig. 6. Spectral change during the irradiation of *cis,cis*-**10** in *n*-hexane (a), *cis,trans*-**10** in *n*-hexane (b) and *trans,trans*-**10** in *n*-hexane (c) after 0, 1, 2, 4, 8, 16, 32, 64, 128, 256, 512 and 1024 s (λ_{ir} = 350 nm, ℓ = 1 cm).

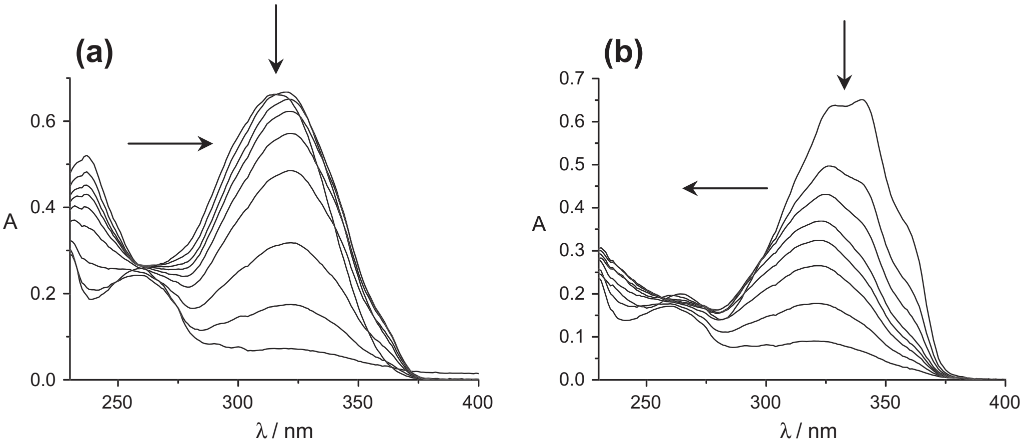


Fig. 7. Spectral change during the irradiation of *cis*-11 in *n*-hexane (a) after 0, 1, 2, 4, 8, 16, 32, 64 and 128 s, and *trans*-11 in *n*-hexane (b) after 0, 1, 2, 4, 8, 16, 32, 64 s ($\lambda_{ir} = 350$ nm, ℓ = 1 cm).

As a part of our increasing interest in the photochemistry of conjugated butadiene systems we extended our research to new chloro derivatives **9**–**12** (Fig. 2). New mono- and dichloro butadienes **9**–**12** were synthesized by Wittig reactions. Compounds **9**–**12** undergo photochemical reactions to give new polycyclic structures. We predicted that electronic and steric effects of one or two chlorine atoms as substituents at different locations in the molecule would provide new, complex polycyclic structures based on the known photochemistry of chloro substituted stilbene derivatives [15–20].

2. Results and discussion

2.1. Synthesis

The starting materials, chloro substituted butadiene derivatives (**9**–**12**) were prepared by Wittig reactions from the corresponding diphosphonium salt and cinnamaldehydes (Scheme 1) [13,14,21,22]. The products were obtained in good yields (51–78%) as mixtures of two (compounds **9** and **11**) or three geometric isomers (compounds **10** and **12**). The syntheses were

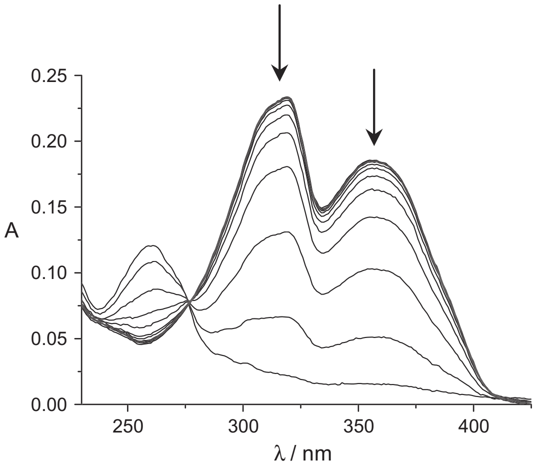


Fig. 8. Spectral change during the irradiation of *trans,trans*-**12** in *n*-hexane after 0, 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024 and 2048 s (λ_{ir} = 350 nm, ℓ = 1 cm).

performed using the corresponding (*Z*) or (*E*) stereoisomers so the second double bond (relative to the *ortho* substituted central benzene ring) in the starting compounds **9**–**12** retains the (*E*) configuration.

Hence, the number of the geometric isomers was reduced and the reaction mixtures contain *cis*- and *trans*-isomers of **9** and **11**, and *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **10** and **12** (only the stereochemistry of the first double bond connected to the *ortho* substituted central benzene ring is fixed).

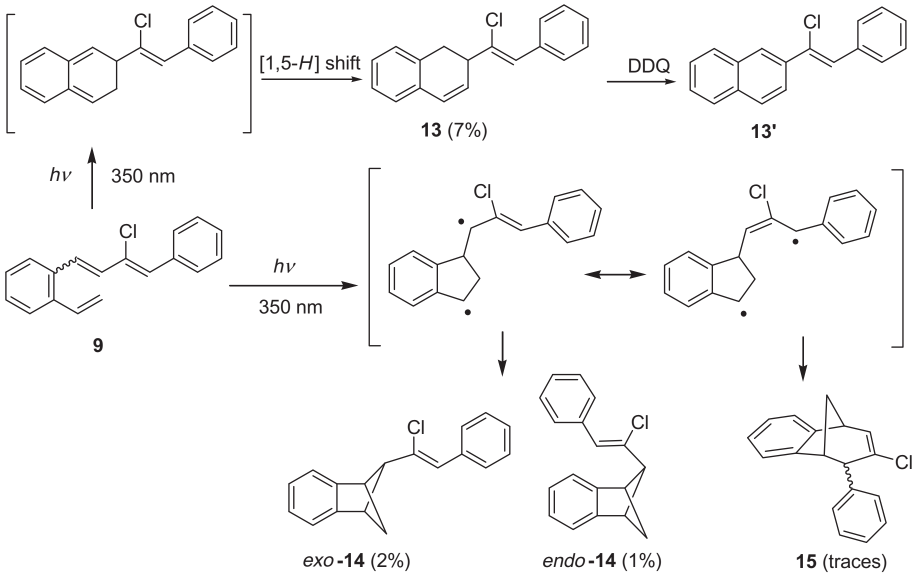
In these new systems with extended conjugation, the influence of chlorine atom at the double bond or at the benzene ring was examined to see whether intramolecular [2 + 2] photocycloaddition was followed by formation of the benzobicyclic structures and/or photoelectrocyclization led to photoproducts possessing six-membered rings. The steric hindrance of the chlorine in **9** (Scheme 2) and **10** should cause larger deviations from planarity [20] than in **11** and **12**, thereby shifting the equilibrium between conformers and altering the reaction pathways and yields.

Although the conformers of each isomer studied in this work may display deviating photoinduced behaviour, similar to some 2-vinylbiphenyls [23], 1,2-dinaphthylethenes [24] and 1-naphthyl-2-phenylethenes [25], deeper investigation of the effects of the conformational diversity within the steric influence of the starting geometric isomers on the reaction pathway was not the aim of this work.

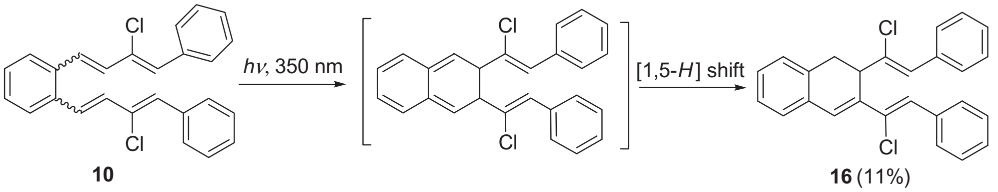
The geometric isomers of **9**–**12** can be easily identified from their ^{1}H NMR spectra by the characteristic vicinal coupling constants of the *cis*- and *trans*-ethylenic protons. According to ^{1}H NMR spectra of the crude reaction mixtures the ratio of *cis*- and *trans*-isomers of **9** was ~1:3 and of **11** was ~1:1, whereas the ratio of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **10** was ~1:6:2. The isomers of **9**–**12** were separated combining column and preparatory thin-layer chromatography on silica gel using petroleum ether as the eluent, completely analysed and identified spectroscopically.

2.2. UV absorption spectra

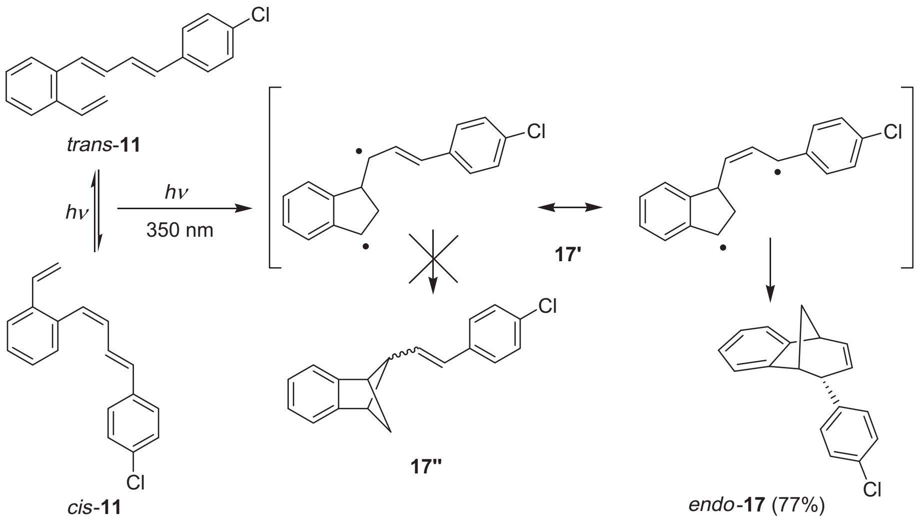
The UV spectra (Figs. 3 and 4) of separated isomers of **9**–**12**, clearly show the substituent and configurational influence on



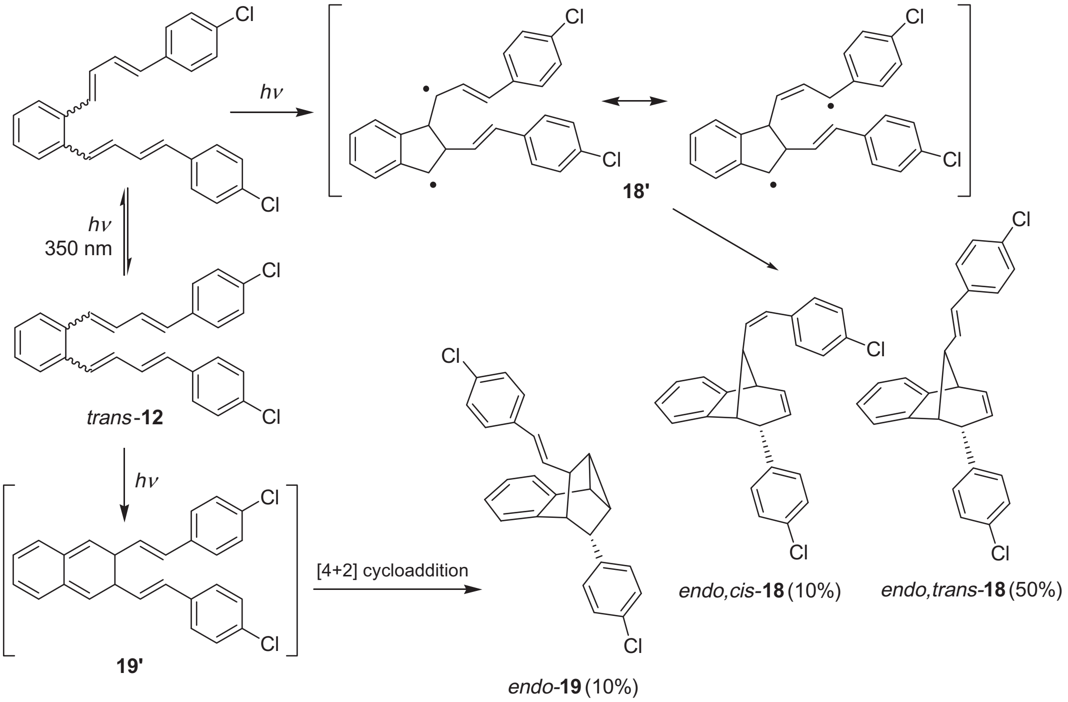
Scheme 3. Proposed mechanism for the photochemistry of the *o*-vinylbutadiene **9**.



Scheme 4. Proposed mechanism for the formation of photoproduct **16**.



Scheme 5. Proposed mechanism for the photochemistry of *p*-chloro-substituted derivative **11**.



Scheme 6. Proposed mechanism for the formation of photoproducts **18** and **19**.

absorption characteristics. As expected, the *trans*-**9** and *trans*-**11** isomers show a bathochromic shift and an increase in molar absorption coefficients relative to the *cis*-isomers due to increased molecule planarity of the *trans* configuration and resultant improved delocalisation of π-electrons (Fig. 3). In the related molecules **9**/**11** or **10**/**12**, with the same configuration but different locations of chlorine atom(s) substitution, compounds **11** and **12** show a bathochromic shift in comparison to **9** and **10**, due to better delocalisation of π-electrons in the absense of the chlorine on the butadiene unit(s) (Figs. 3 and 4).

The separated isomers of **9**–**12** were irradiated and the reaction course followed by UV spectroscopy (Figs. 5–8). For all compounds, the longest-wavelength absorption band gradually disappeared upon irradiation.

These spectral changes generally indicate that the conjugation between the phenyl groups *via* the butadiene link was interrupted by the photolysis, and that the electronic systems of the aromatic rings were isolated.

In numerous cases, as the initial changes of the absorption spectra indicate (Figs. 6a,b and 7a,b), photoisomerization is one of the primary process, which is either followed or accompanied by a competitive photochemical reaction [26,27]. It is difficult to discuss about the composition of the photostationary mixture because of unsymmetrical structure of the starting compounds **9**–**12** and possibility of existence and interconversion of the configurational isomers.

2.3. Photochemistry

The preparative irradiation experiments of **9**–**12** were performed in petroleum ether solutions under anaerobic conditions at 350 nm and at low concentrations, ~10^{-3} M. Depending on

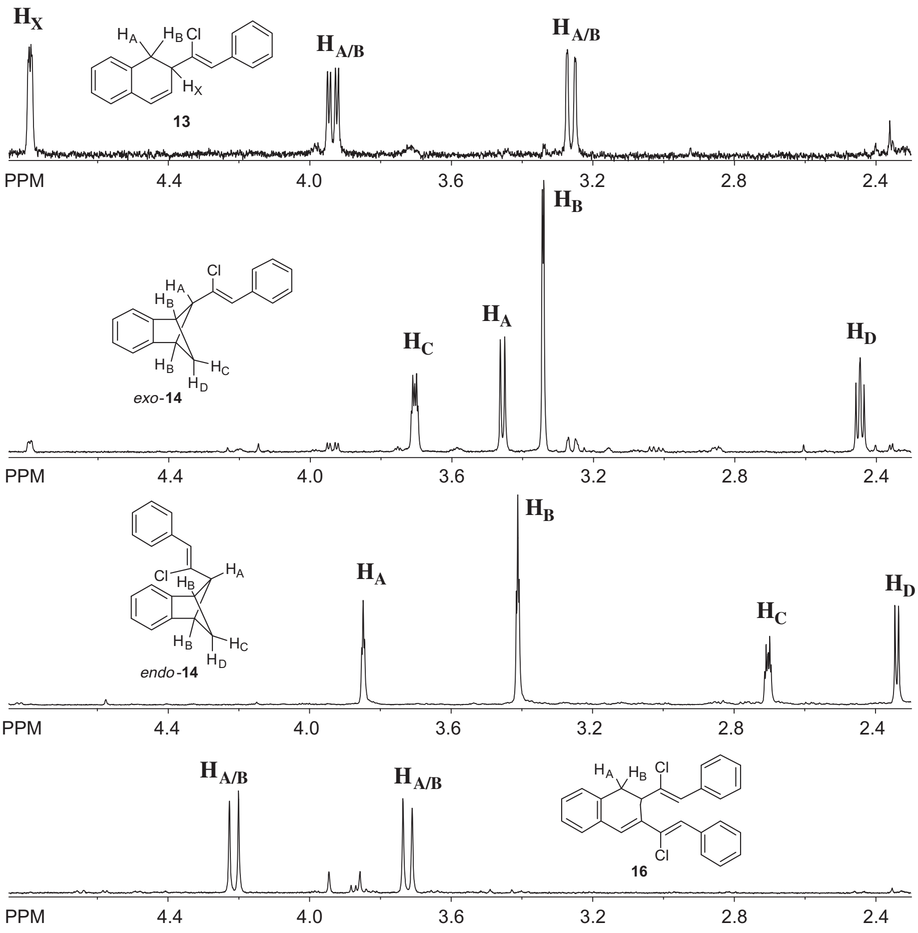


Fig. 9. Aliphatic region of the ^{1}H NMR spectra: (a) **13**; (b) *exo*-**14**; (c) *endo*-**14**; and (d) **16** ($CDCl_3$, 300 MHz).

the structure of the starting compound, different types of photoproducts were isolated and identified. The formation of the photoproducts was generally accompanied by the formation of polymeric products which were not investigated.

On preparative irradiation of 2-chloro-1-(*o*-vinylphenyl)-4-phenylbutadiene derivative (**9**) at 350 nm, cyclohexadiene derivative **13** was isolated as the main photoproduct (7%). This product results from the primary electrocyclic ring closure process characteristic for 1,3,5-hexatriene (Scheme 3) [28,29]. The proposed reaction mechanism for transformation of the *o*-butadienylstyrene **9** involves a six-membered ring-closure followed by sigmatropic 1,5H-shift to give the stable photoproduct **13**. The reaction is not selective and several minor products (Scheme 3) *exo*-**14** (2%), *endo*-**14** (1%) and **15** (in traces) were also formed during the irradiation of **9** (Scheme 3). The photoproducts **13**, *exo*-**14** and *endo*-**14** were separated by column chromatography on silica gel and the structures deduced unequivocally from spectral studies and from characteristic NMR data after the dehydrogenation reaction with DDQ to fully aromatized structure **13′** [30].

Product **15** was seen only in enriched chromatographic fractions and was identified according to the very well resolved six-proton-pattern in the ^{1}H NMR spectrum and by the characteristic couplings for this type of rigid bicyclo[3.2.1]octadienes [13,14]. It might be assumed that the 1,4-ring closure to benzobicyclo[2.1.1]hexene derivative **14** could thermally revert to **9** and subsequently give the more stable product **15**, but that did not happen. The less stable benzobicyclo[3.1.0]hexene structure formed due to the electronic and steric influence of the chlorine on the double bond precluding the allyl system resonance in the intermediate.

In an effort to study the influence of extended conjugation in our systems to the course of the photoreaction, we introduced a second styryl substituent at the β-position of the vinyl group, and synthesized the new dichloro-dibutadiene derivative **10**. Photolyses of these isomers display different characteristics at the initial period of irradiation, depending on the configuration of the starting isomer. These conformational predictions were confirmed upon product analysis. Only one conformer of the *trans*,-*trans*-isomer is favoured and the unique final product **16** was formed in 11% yield (Scheme 4). The remaining product mass was tarry material. The proposed mechanism involves a six-membered ring-closure followed by sigmatropic 1,5H-shift to give the stable photoproduct **16** (Scheme 4). In comparison with the corresponding monosubstituted derivative **9**, the photoreaction is more selective giving only one photoproduct.

Preparative irradiation of *p*-chloro-phenylbutadiene derivative **11** at 350 nm, results in the formation of bicyclo[3.2.1]octadiene structure *endo*-**17**, in a very good 77% yield (Scheme 5). The stereoselective formation of *endo*-benzobicyclic structure could be explained by initial intramolecular cycloaddition and formation of resonance-stabilized intermediate **17′** followed by 1,6-ring closure (Scheme 5), as seen previously in the photochemical reactions of *β*-heteroaryl substituted *o*-divinylbenzenes [2,4,6,8] and butadienylstilbenes [13,14]. It might be assumed that even if the 1,4-ring closure [2,26] to benzobicyclo[2.1.1]hexene derivative **17″** is operating the formed derivative **17″** could thermally reverse to

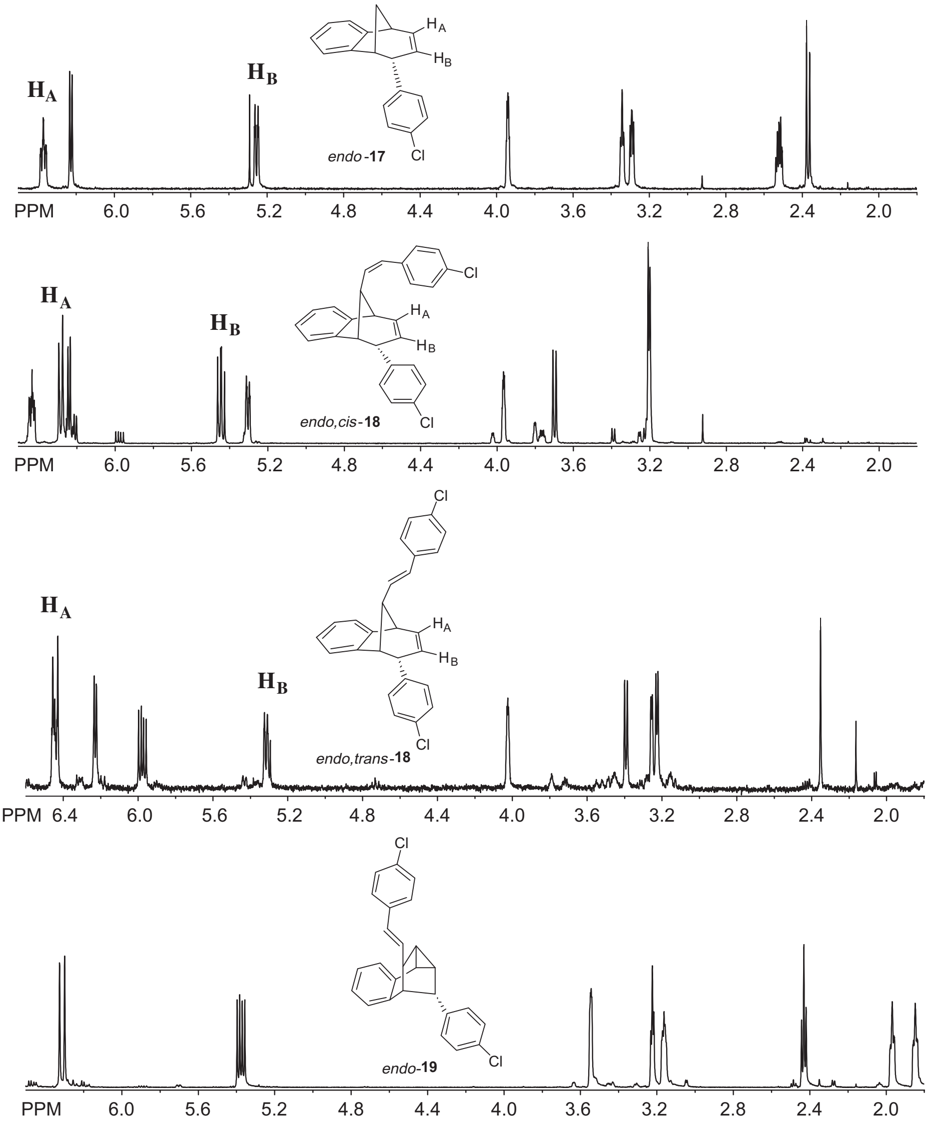


Fig. 10. Part of the ^{1}H NMR spectra: (a) bicyclic *endo*-**17**; (b) bicyclic *endo,cis*-**18**; (c) bicyclic *endo,trans*-**18, and** (d) tricyclic *endo*-**19**; ($CDCl_3$, 300 MHz).

intermediate **17**′ and subsequently give the more stable product *endo*-**17**. The ring closure predominantly gives *endo*-isomer. The stereoselectivity of the reaction of *o*-butadienylstyrene **11** and preferable ring closure to *endo*-isomer can be ascribed to the stabilization of the transition state in *endo*-orientation by the strong attractive intramolecular π–π interactions of the benzo-*p*-chlorophenyl groups [31–33].

Contrary to the α-dichloro-substituted dibutadiene derivative **10**, introduction in compound **11** of the second *p*-chlorostyryl substituent at the β-position of the vinyl group, gaining new *p*-dichloro-dibutadiene derivative **12** resulted in different photochemical behaviour (Scheme 6). On irradiation of the mixture of isomers of **12**, under the same conditions as for the starting material **10**, photoisomerization to *trans,trans*-**12** is the primary process followed by two competing processes, photocycloaddition to **18** (through the initial five-membered-ring-closure *via* **18**′, followed by intramolecular trapping of the formed biradical) or by electrocyclic six-membered-ring-closure to **19** *via* **19**′. During the column chromatography in the first fractions *endo*- and *exo*-**18** photoproducts were isolated and followed by benzotricyclic compound *endo*-**19** in the last fractions. High-molecular-weight products remained on the column. The dihydronaphthalene intermediate **19**′, formed by 6π electrocyclization process, is intramolecularly trapped by one of the styryl bonds giving the polycyclic compound **19** (Scheme 6).

The isolated photoproducts **13**–**19** were completely characterized by spectroscopic methods (see Section 4). The ^{1}H NMR spectrum of **13** shows the characteristic ABX pattern between 3.2 and 4.8 ppm (Fig. 9a). The ^{1}H NMR spectrum of isolated photoproduct **16** shows two doublets between 3.7 and 4.3 ppm with geminal coupling constants (Fig. 9d) in the aliphatic region and the singlet for H_X proton is deshielded to 5.9 ppm (see Section 4). The aliphatic regions of the ^{13}C NMR spectra of **13** and **16** are very similar with two signals assigned to one CH and one CH_2 group.

The very well resolved seven-proton-pattern in the ^{1}H NMR spectrum of the photoproduct *endo*-**17** between 2.3 and 6.4 ppm unmistakably point to the benzobicyclo[3.2.1]octadiene structure (Fig. 10). The multiplets in the lower field between 5.2 and 6.4 ppm are assigned to the A and B alkenyl protons. One of the aromatic protons of the benzo-moiety is shifted to higher field due to the anisotropic effect of the other aromatic ring, *endo*-substituted (see Section 4) and indicating the same structure. Similar spectra is obtained in the case of the main photoproducts *endo*-**18** which differ only in the configuration of the styryl double bond attached to the methano-bridge. The benzotricyclic structure *endo*-**19** has a completely different pattern in ^{1}H NMR spectrum. All six

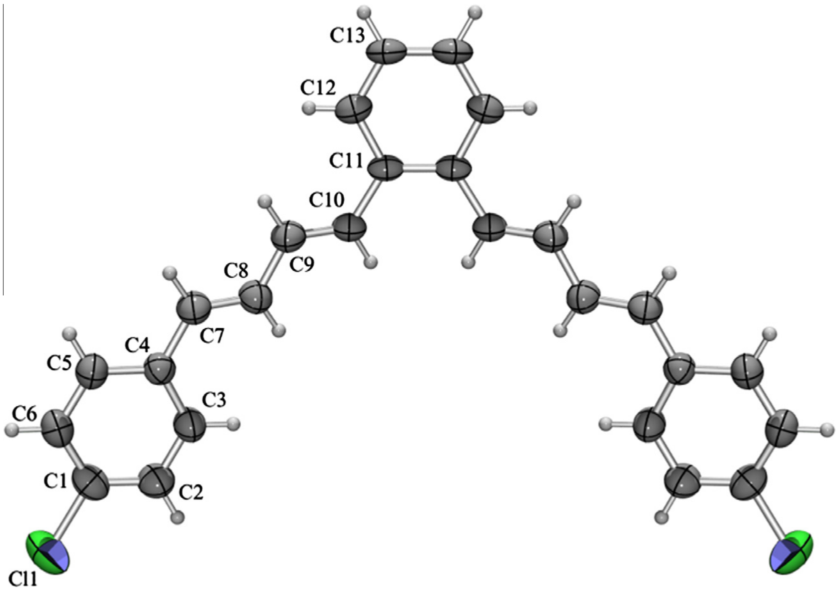


Fig. 11. ORTEP-3 [34] drawing of a molecule of *trans,trans*-**12**. Displacement ellipsoids are drawn for the probability of 30% and hydrogen atoms are shown as spheres of arbitrary radii.

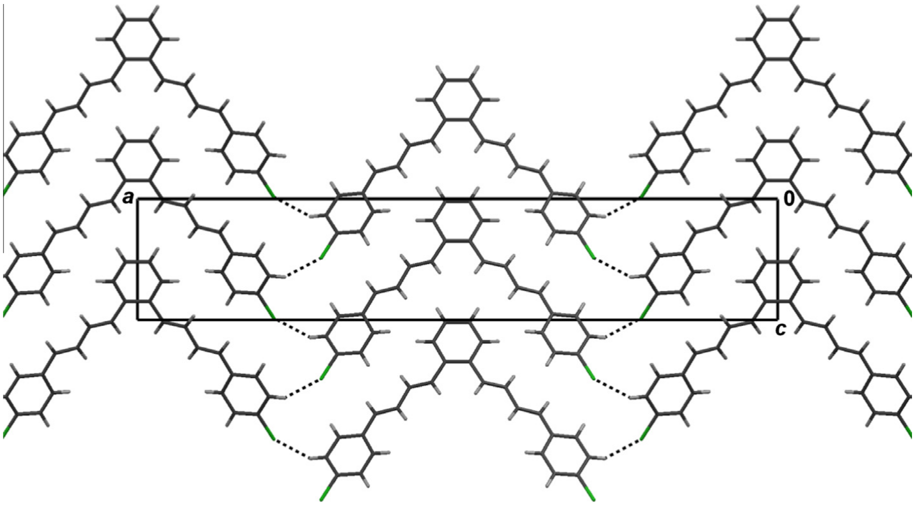


Fig. 12. Crystal packing of *trans,trans*-**12** viewed in the direction [0 1 0].

protons appear between 1.6 and 3.6 ppm with the corresponding multiplicity (see Section 4, Fig. 10). MS spectra data was used to determine the presence of one or two chlorine atoms in the molecule (see Fig. 11).

2.4. X-ray study

The structure of the *trans,trans*-isomer of starting compound **12** was finally confirmed by X-ray analysis. The observed solid-state conformation corresponds with the conformation required for the formation of the main photoproduct **18** with a benzobicyclo[3.2.1]octadiene skeleton. The molecular symmetry of *trans,trans*-**12** is Cs, with crystallographic mirror plane passing through the central phenyl ring (i.e. midpoints of C13–C13^i and C11–C11^i bonds). The only intermolecular interaction in the crystals are rather long C6–H6···Cl1 bonds (Fig. 12; d(C–H) = 0.93 Å; d(H···Cl) = 3.04 Å; d(C···Cl) = 3.823(8) Å; (C–H–Cl) = 142°; symmetry operator i) 1/2 − x, −y, −1/2 + z), which link the molecules into layers parallel to the plane (1 0 1). There are only dispersion interactions between the layers.

Concerning the mechanistic considerations, the formation of the six-membered ring in **13** (Scheme 3) is more plausible, given the steric hindrance of the chloro substituent,[23] in contrast with unsubstituted derivative **1** providing the benzobicyclic structure *endo*-**5** as the only photoproduct (Fig. 1). The initial intramolecular photocycloaddition from the other conformer, leading to the bicyclic structures **14** and **15**, is a less favourable process than the initial 6π electrocyclization leading to **13**. We assume that due to the changes induced by the steric effect of the chlorine in the excited state of the **9**, delocalization through the non-planar part of the molecule, which contains the chloro substituent, is generally not favourable. The similar effect can be assumed in the case of α-dichloro-substituted butadiene **10**. Mono- or di-*p*-chloro-substituted butadienes **11** and **12** gave intramolecular photoadducts as the main structures in the photoreaction in the absence of the steric hindrance of the chlorine (as in the case of **9** and **10**). The shift of the conformer equilibrium affects the reaction pathway and final yields. Of the α-chloro substituted compounds examined, **10** was the most selective but with relatively low yield for the single electrocyclization product. For the *p*-chloro substituted derivatives, **11**

Table 1
Crystallographic, data collection and structure refinement details.

Compound	*trans,trans*-**12**
Empirical formula	$C_{26}H_{20}Cl_2$
Formula wt. (g mol^{-1})	201.66
Crystal dimensions (mm)	0.12 × 0.10 × 0.09
Space group	$P\ m\ n\ 2_1$
a (Å)	36.487(2)
b (Å)	4.0092(2)
c (Å)	6.8891(3)
α (°)	90
β (°)	90
γ (°)	90
Z	4
V (Å^3)	1007.76(9)
D_{calc} (g cm^{-3})	1.329
μ (mm^{-1})	2.943
Θ range (°)	4.85–75.66
T (K)	293(2)
Radiation wavelength	1.54179 (Cu Kα)
Diffractometer type	Xcalibur Nova
Range of h, k, l	$-42 < h < 45$ $-5 < k < 3$ $-8 < l < 5$
Reflections collected	2436
Independent reflections	1504
Observed reflections ($I \geqslant 2\sigma$)	1458
Absorption correction	Multi-scan
R_{int}	0.0319
R (F)	0.0741
R_w (F^2)	0.2110
Goodness of fit	0.967
H atom treatment	Constrained
No. of parameters	128
No. of restraints	1
$\Delta\rho_{max,}$ $\Delta\rho_{min}$ (eÅ^{-3})	0.352; −0.320

gave one stereoisomer of benzobicyclo[3.2.1]octadiene skeleton, in very good yield. The electronic effect of the chlorine substituent(s) greatly influenced the product yields. Methyl and chloro substituents have similar steric requirements but very different electronic effects. In comparison with the methyl analogues **2** (Fig. 1) the overall yield for the analogous electrocyclization products is lower than from **9**. The chlorine atoms reduce the resonance of the intermediate more than a methyl group in the same position, directing rather the formation of bicyclo[2.1.1]hexene as the minor cycloadduct **14**, instead the bicyclo[3.2.1]octadiene skeleton **15**. The α-dichloro derivative **10** selectively gives the electrocyclization product **16** (Scheme 4) whereas the corresponding dimethyl derivative **4** (Fig. 1) shows only geometrical isomerization due to the bulky methyl substituents. The unsubstituted butadienylstyrene **1** gave the intramolecular photocycloaddition product in 90% yield the corresponding *p*-chloro substituent in **11** gave the same type of the product **17** but in lower yield. The photoreaction of *p*-dichloro substituted compound **12**, was less selective than the unsubstituted analogue **3**. The same methodology applied earlier at 300 nm (instead 350 nm) to the chloro-vinylstilbenes [3–7], gave completely different photoproducts. The reaction mechanism at 300 nm was explained by primary cleavage of the C–Cl bond or HCl elimination from the molecule and the obtained unsubstituted compounds reacted by known mechanism without the influence of chlorine substituent.

3. Conclusions

The initial compounds **9**–**12** display diverse photochemical behaviour. In dilute solution, besides unidentified degradation and high-molecular-weight products, photoreaction of *o*-butadienylstyrene **9** leads to the major product **13** generated by electrocyclic ring closure while the intramolecular cycloaddition into benzobyciclo[2.1.1]hexene products **14** and benzobyciclo[3.2.1]octadiene product **15** are less favourable. The photoreaction mechanism of molecule **9** includes electrocyclic ring closures and hydrogen shift, which selectively leads only to dihydronaphthalene derivative **13**. On the other hand, the irradiation of *o*-butadienylstyrene **11** preferentially leads to an intramolecular cycloaddition where the major photoproduct is benzobyciclo[3.2.1]octadiene derivative *endo*-**17**. In dichloro-substituted conjugated compounds **10** and **12**, the position of the chlorine atoms directs the dominant photoreaction pathway based on the conformation of the *trans,trans*-isomers of **10** or **12**. Four molecules of similar structures showed dramatically different photoinduced behaviour and demonstrate how changes in the position of the chlorine substituent direct the photochemistry of these related compounds. Chlorine atoms can affect on mono- and dibutadiene unit through mesomeric and inductive effects. Understanding the dominant effects of chlorine substituents in photochemical reactions of related new butadiene derivatives and explanation of reaction mechanisms in obtaining photoproducts, makes the synthesis of these systems suitable for routing photoreaction towards various interesting structures for further transformations and functionalization using simple approach with light as reagent.

4. Experimental section

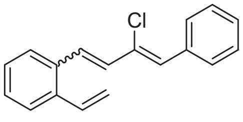
4.1. General information

The ^{1}H spectra were recorded on a spectrometer at 600 MHz. The ^{13}C NMR spectra were registered at 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY experiments. UV spectra were measured on a UV/VIS Cary 50 spectrophotometer. IR spectra were recorded on a FTIR–ATR (film). Irradiation experiments were preformed in a quartz vessel in petroleum ether solution in a photochemical reactor equipped with 3000 Å lamps. All irradiation experiments were carried out in deaerated solutions by bubbling a stream of argon prior to irradiation. Melting points were obtained using apparatus equipped with microscope and are uncorrected. HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyzer), equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive (H+) or negative (H−) ion reflector mode. Silica gel (0.063–0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed silica gel 60 F_{254} plates. Solvents were purified by distillation.

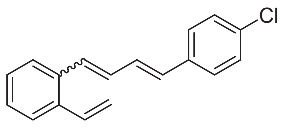
α-Chloro-(*Z*)-cinnamaldehyde and *p*-chloro-(*E*)-cinnamaldehyde were obtained from a commercial source, *β*,*β*-*o*-xylyl(ditriphenylphosphonium) dibromide was prepared from *o*-xylyldibromide and triphenylphosphine in dimethylformamide.

4.2. General method for the synthesis of **9** and **11**

Starting compounds **9** and **11** were prepared by Wittig reaction from *o*-xylylenebis(triphenylphosphonium bromide) and the corresponding aldehydes, α-chloro-(*Z*)-cinnamaldehyde and *p*-chloro-(*E*)-cinnamaldehyde. To a stirred solution of the triphenylphosphonium salt (0.010 mol) and the corresponding aldehyde (0.011 mol) in absolute ethanol (200 mL), a solution of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 h at RT. Under the stream of dry nitrogen gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 1.5 g) was introduced and the next quantity of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. The reaction was completed within 3–4 h (usually was left to stand overnight). After removal of the solvent, the residue was worked up with water and toluene. The toluene extracts were dried (anhydrous $MgSO_4$) and concentrated. The crude reaction mixture was purified and the isomers of products **9** (51%) and **11** (78%) were separated by repeated column chromatography on silica gel using petroleum ether as the eluent. The first fractions yielded *cis*- and the last fractions *trans*-isomers.



9



11

cis-**9**: 13%; R_f 0.35 (petroleum ether); colourless oil; UV (96% EtOH) λ_{max} (logε) 227 (4.38); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.51 (dd, J = 7.7; 1.5 Hz; 1H), 7.45 (d, J = 7.7 Hz, 2H), 7.32–7.26 (m, 4H), 7.24–7.22 (m, 4H), 7.19 (dt, J = 7.7; 1.5 Hz, 1H), 6.92 (dd, J = 17.5; 10.9 Hz, 1H), 6.68 (d, J = 12.0 Hz, 1H), 6.48 (s, 1H), 6.32 (dd, J = 12.0; 0.9 Hz, 1H), 5.68 (dd, J = 17.5; 1.2 Hz, 1H), 5.31 (dd, J = 10.9; 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 132.6 (s), 134.6 (s), 134.5 (d), 134.3 (s), 130.3 (d), 130.1 (d), 129.0 (d), 128.8 (d), 128.7 (d), 127.6 (2d), 127.4 (2d), 127.2 (d), 126.9 (d), 125.0 (d), 115.3 (t) (too small quantities for detection of all singlets); IR ν_{max} 3056, 1601, 1453, 698.

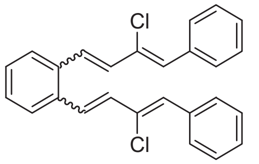
trans-**9**: 38%; R_f 0.32 (petroleum ether); colourless crystals; mp 46 °C; UV (96% EtOH) λ_{max} (logε) 319 (4.49); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 7.6 Hz, 2H), 7.53–7.46 (m, 2H), 7.43–7.35 (m, 3H), 7.09 (dd, J = 17.4; 10.9 Hz, 1H), 6.83 (d, J = 15.2 Hz, 1H), 6.78 (s, 1H), 5.66 (dd, J = 17.4; 1.3 Hz, 1H), 5.39 (dd, J = 10.9; 1.3 Hz, 1H); ^{13}C NMR (C_6H_6, 150 MHz) δ 136.6 (s), 134.7 (s), 134.3 (d), 134.3 (s). 129.8 (d), 129.3 (d), 129.1 (d), 129.0 (d), 128.9 (s), 128.0 (d), 127.9 (d), 127.8 (2d), 127.6 (2d), 126.3 (d), 126.0 (d), 116.1 (t); IR ν_{max} 3058, 1694, 1491, 754; HRMS for $C_{18}H_{15}Cl$: $M^+_{\text{calcd.}}$ 266.0857; M^+_{found} 266.0848 (for a mixture of isomers of **9**).

cis-**11**: 45%; R_f 0.69 (petroleum ether/dichloromethane = 9:1); colourless oil; UV (96% EtOH) λ_{max} (logε) 317 (4.43), 237 (4.33); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.56 (dd, J = 8.0; 2.3 Hz, 1H), 7.30–7.28 (m, 3H), 7.26–7.23 (m, 4H), 6.97 (dd, J = 15.4; 11.0 Hz, 1H), 6.90 (dd, J = 17.5; 11.1 Hz, 1H), 6.64 (d, J = 11.2 Hz, 1H), 6.61 (d, J = 15.4 Hz, 1H), 6.47 (t, J = 11.2 Hz, 1H), 5.69 (d, J = 17.5 Hz, 1H); 5.29 (d, J = 11.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 136.5 (s), 135.8 (2s), 135.6 (s), 135.1 (d), 133.0 (d), 130.9 (d), 130.2 (d), 129.9 (d), 128.7 (2d), 127.7 (2d), 127.6 (d), 127.4 (d), 126.1 (d), 125.8 (d), 115.7 (t); IR ν_{max} 3025, 1489, 1091, 771.

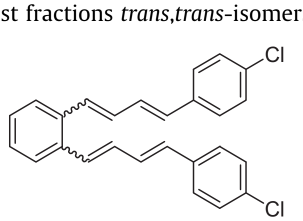
trans-**11**: 33%; R_f 0.66 (petroleum ether/dichloromethane = 9:1); colourless crystals; mp 110–113 °C; UV (96% EtOH) λ_{max} (logε) 340 (4.57), 329 (4.56, sh), 265 (4.53); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.51 (dd, J = 7.3; 1.7 Hz, 1H), 7.45 (dd, J = 7.3; 1.7 Hz, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.27–7.23 (m, 2H), 7.06 (dd, J = 17.3; 11.0 Hz, 1H), 6.98 (d, J = 15.3 Hz, 1H), 6.95 (dd, J = 15.4; 10.5, 1H), 6.82 (dd, J = 15.4; 10.5 Hz, 1H), 6.61 (d, J = 15.4 Hz, 1H), 5.63 (dd, J = 17.3; 1.2 Hz, 1H), 5.36 (dd, J = 11.0; 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 135.9 (s), 135.4 (s), 134.7 (s), 134.4 (d), 132.7 (s), 131.0 (d), 130.5 (d), 130.4 (d), 129.6 (d), 128.3 (2d) 127.3 (d), 127.2 (d), 127.0 (2d), 126.3 (d), 125.4 (d), 116.1 (t); IR ν_{max} 2923, 1739, 1489, 1092, 986; HRMS for $C_{18}H_{15}Cl$: $M^+_{\text{calcd.}}$ 266.0857; M^+_{found} 266.0867 (for a mixture of isomers of **11**).

*4.3. General method for the synthesis of **10** and **12***

To a stirred solution of the triphenylphosphonium salt (0.005 mol) and the corresponding aldehyde (0.011 mol) in absolute ethanol (100 mL) the solution of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. The reaction was completed within 3–4 h (usually was left to stand overnight). After removal of the solvent, the residue was worked up with water and toluene. The toluene extracts were dried (anhydrous $MgSO_4$) and concentrated. The crude reaction mixture was purified and the isomers of products **10** (55%) and **12** (50%) were separated by repeated column chromatography on silica gel using petroleum ether as the eluent. The first fractions yielded *cis*,*cis*-, *cis*,*trans*- and the last fractions *trans*,*trans*-isomers.



10



12

cis,*cis*-**10**: 6%; R_f 0.79 (petroleum ether/dichloromethane = 7:3); colourless crystals; mp 65–66 °C; UV (96% EtOH) λ_{max} (logε) 251 (4.36); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.44–7.40 (m, 6H), 7.27–7.24 (m, 4H), 7.23–7.13 (m, 2H), 7.18–7.15 (m, 2H), 6.61 (d, J = 12.0 Hz, 2H), 6.52 (s, 2H), 6.29 (dd, J = 12.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 134.9 (s), 134.2 (s), 130.0 (d), 129.9 (d), 128.8 (d), 128.7 (2d), 128.6 (d), 127.7 (s), 127.6 (2d), 127.5 (d), 126.8 (d); IR ν_{max} 3022, 1619, 1491, 1081, 688.

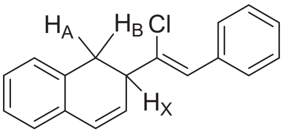
cis,*trans*-**10**: 37%; R_f 0.76 (petroleum ether/dichloromethane = 7:3); colourless oil; UV (96% EtOH) λ_{max} (logε) 319 (4.43); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.72 (d, J = 7.3 Hz, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 7.3 Hz, 2H), 7.39–7.33 (m, 3H), 7.31–7.19 (m, 7H), 6.87 (d, J = 15.1 Hz, 1H), 6.75 (s, 1H), 6.73 (d, J = 12.1 Hz, 2H), 6.51 (s, 1H), 6.39 (dd, J = 12.1; 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.1 (s), 134.89 (s), 134.84 (s), 131.68 (s), 131.62 (s), 131.4 (s), 131.1 (d), 130.5 (d), 130.0 (d), 129.9 (d), 129.77 (2d), 129.71 (2d), 129.4 (d), 129.3 (2d), 128.8 (d), 128.3 (2d), 128.2 (d), 128.1 (2d), 128.0 (d), 127.8 (d), 127.7 (d), 125.8 (d).

trans,*trans*-**10**: 12%; R_f 0.73 (petroleum ether/dichloromethane = 7:3); colourless oil; UV (96% EtOH) λ_{max} (logε) 306 (4.00); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.75 (d, J = 7.5 Hz, 4H), 7.53–7.51 (m, 2H), 7.44 (d, J = 15.3 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.31–7.27 (m, 4H), 6.84 (d, J = 15.3 Hz, 2H), 6.79 (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 134.9 (s), 134.5 (s), 130.8 (s), 130.1 (d),129.2 (2d), 129.1 (d), 129.0 (d), 127.8 (2d), 127.7 (d), 127.6 (d), 126.5 (d); IR ν_{max} 3021, 1445, 1143, 950, 690; HRMS ($-H^+$) for $C_{26}H_{20}Cl_2$: $M^+_{\text{calcd.}}$ 401.0869; M^+_{found} 401.0888 (for a mixture of isomers of **10**).

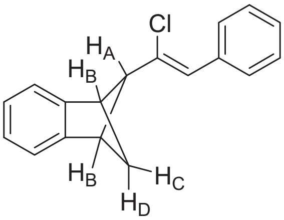
trans,*trans*-**12**: 50%; R_f 0.88 (petroleum ether/dichloromethane = 1:1); yellow crystals; mp 262 °C; UV (96% EtOH) λ_{max} (logε) 355 (4.17), 319 (4.27); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.52 (d, J = 9.1 Hz, 1H), 7.38 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.28–7.24 (m, 1H), 7.03 (d, J = 15.3 Hz, 1H), 6.98 (dd, J = 15.5; 10.5 Hz, 1H), 6.84 (dd, J = 15.3; 10.5 Hz, 1H), 6.64 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 135.3 (s), 135.0 (s), 132.7 (s), 131.2 (d), 130.8 (d), 130.3 (d), 129.5 (d), 128.4 (2d), 127.3 (d), 127.0 (2d), 125.8 (d); IR ν_{max} 3040, 1742, 1488, 1089, 974; HRMS ($+H^+$) for $C_{26}H_{20}Cl_2$: $M^+_{\text{calcd.}}$ 403.1015; M^+_{found} 403.1019 (for a mixture of isomers of **12**).

*4.4. Irradiation experiments of **9** and **11***

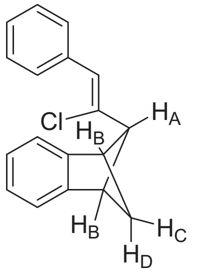
A mixture of *cis*- and *trans*-isomers of **9** or **11** in petroleum ether (3.7×10^{-3} M) was purged with argon for 20 min and irradiated at 350 nm in a Rayonet reactor (12 lamps) in a Quartz vessel for 16 h. After irradiation the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The photoproducts **13**–**15** obtained from **9** or the photoproduct **17** obtained from **11** were isolated from the enriched first chromatographic fractions followed by a mixture of several unidentified products (<2%). High-molecular-weight products remained on the column.



13



exo-**14**

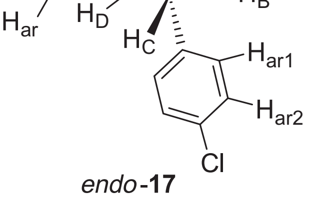


endo-**14**

13: 7%; R_f 0.32 (petroleum ether); colourless crystals; mp 60–62 °C; UV (96% EtOH) λ_{max} (logε) 325 (3.32), 317 (3.34), 311 (3.35), 292 (3.40), 281 (3.46), 270 (3.43), 229 (4.33); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.89 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.52–7.42 (m, 3H), 7.34–7.19 (m, 6H), 4.80–4.77 (dd, J = 5.1; 2.0 Hz, H_X, 1H), 3.96–3.91 (dd, J = 13.6; 5.1 Hz, H_A/H_B, 1H), 3.28–3.24 (dd, J = 13.6; 2.0 Hz, H_A/H_B, 1H,); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 144.6 (s), 142.9 (s), 141.2 (s), 133.4 (s), 129.6 (d), 128.4 (2d), 128.1 (d), 127.0 (2d), 126.5 (d), 126.4 (d), 125.1 (d), 122.2 (d), 121.3 (d), 46.6 (d), 38.2 (t); IR ν_{max} 2922, 1656, 1453, 1028, 814; HRMS for $C_{18}H_{15}Cl$: $M^+_{calcd.}$ 266.0857; M^+_{found} 266.0870.

exo-**14**: 2%; R_f 0.28 (petroleum ether); colourless oil; UV (96% EtOH) λ_{max} (logε) 317 (3.64), 281 (3.71, sh), 273 (6700, sh), 249 (17,476), 229 (23,231); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.50–7.46 (m, 2H), 7.35–7.28 (m, 4H), 7.20–7.24 (m, 2H), 7.01–6.98 (m, 2H), 3.72–3.68 (m, 1H, H_C), 3.46 (d, J_{AD} = 7.6 Hz, 1H, H_A), 3.34 (d, J_{BC} = 2.4 Hz, 2H, H_B), 2.45 (dd, J_{CD} = J_{AD} = 7.6 Hz, 1H, H_D); IR ν_{max} 2923, 1645, 1492, 1070, 754; HRMS for $C_{18}H_{15}Cl$: $M^+_{calcd.}$ 266.0857; M^+_{found} 266.0851.

endo-**14**: 1%; R_f 0.24 (petroleum ether); colourless crystals; mp 60 °C; UV (96% EtOH) λ_{max} (logε) 317 (3.43), 281 (3.56), 273 (3.61), 247 (4.07), 232 (4.05); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.27–7.24 (m, 2H), 7.17–7.12 (m, 4H), 7.05–7.00 (m, 4H), 3.85 (t, J_{AB} = 2.4 Hz, 1H, H_A), 3.41 (t, J_{AB} = 2.4 Hz, 2H, H_B), 2.72–2.69 (m, 1H, H_C), 2.34 (d, J_{CD} = 6.1 Hz, 1H, H_D); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 149.5 (s), 138.3 (s), 135.4 (s), 133.4 (s), 131.1 (d), 127.8 (d), 127.8 (d), 127.5 (2d), 127.1 (2d), 124.5 (d), 124.0 (2d), 119.9 (d), 59.4 (t), 50.4 (d); IR ν_{max} 2924, 1490, 753; HRMS for $C_{18}H_{15}Cl$: $M^+_{calcd.}$ 266.0857; M^+_{found} 266.0857.

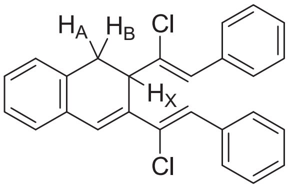


endo-**17**

endo-**17**: 77%; R_f 0.66 (petroleum ether/dichloromethane = 9:1); colourless oil; UV (96% EtOH) λ_{max} (logε) 276 (3.19), 268 (3.22), 224 (4.20, sh); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.14 (d, J = 8.4 Hz, 2H, H_{ar2}), 7.12 (d, J = 7.3 Hz, 1H), 7.03 (td, J = 7.4; 1.0 Hz, 1H), 6.84 (td, J = 7.4; 1.0 Hz, 1H), 6.65 (d, J = 8.3 Hz, 2H, H_{ar1}), 6.40–6.35 (m, 1H, H_A), 6.23 (d, J = 7.3 Hz, 1H, H_{ar}), 5.25 (ddd, J = 9.6; 4.0; 1.9 Hz, 1H, H_B), 3.96–3.92 (m, 1H), 3.34 (t, J = 9.4; 4.7 Hz, 1H), 3.29 (dd, J = 6.1; 4.7 Hz, 1H), 2.54–2.50 (m, 1H, H_F), 2.37 (d, J = 10.0 Hz, 1H, H_G); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 140.6 (s), 137.3 (s), 132.9 (s), 130.9 (s), 134.7 (d), 129.2 (2d), 127.3 (d), 125.7 (d), 125.6 (d), 125.4 (2d), 124.7 (d), 119.7 (d), 48.0 (d), 45.3 (d), 43.7 (t), 39.9; IR ν_{max} 2950, 1490, 1090, 752; HRMS ($-H^+$) for $C_{18}H_{15}Cl$: $M^+_{calcd.}$ 265.0789; M^+_{found} 265.0786.

*4.5. Irradiation experiments of **10** and **12***

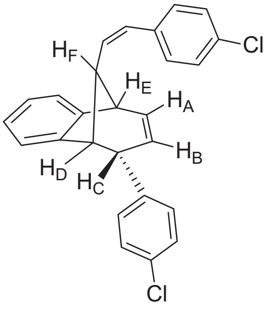
A mixture of *cis,cis-*, *cis,trans-* and *trans,trans*-isomers of **10** or **12** in petroleum ether (2.2×10^{-3} M) was purged with argon for 20 min and irradiated at 350 nm in a Rayonet reactor (**10**: 12 lamps; **12**: 16 lamps) in a Quartz vessel for 16 h (**10**) or 65 h (**12**). After irradiation the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether/dichloromethane (4:1) as the eluent. The photoproducts **16** (from **10**), *endo,cis*-**18**, *endo,trans*-**18** and *endo*-**19** (from **12**) were isolated from the enriched first chromatographic fractions followed by a mixture of several unidentified products (<2%). High-molecular-weight products remained on the column.



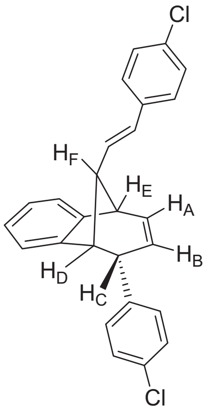
16

16: 11%; R_f 0.71 (petroleum ether/dichloromethane = 4:1); colourless oil; UV (96% EtOH) λ_{max} (logε) 227 (4.52), 272 (3.90, sh), 283 (3.80), 294 (3.71); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.29 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.59–7.54 (m, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.07 (t, J = 7.1 Hz, 2H), 6.64 (s, 1H), 6.61 (s, 1H), 6.28 (s, 1H), 5.97 (s, 1H, H_X), 4.21 (d, J = 15.4 Hz, 1H, $H_{A/B}$), 3.72 (d, J = 15.4 Hz, 1H, $H_{A/B}$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 144.8 (s), 142.2 (s), 137.3 (s), 137.1 (s), 133.2

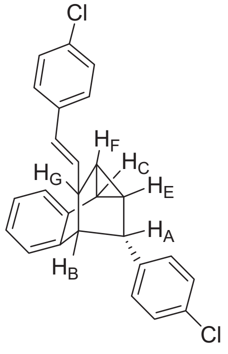
(s), 132.8 (s), 132.1 (d), 131.3 (s), 131.1 (d), 129.9 (d), 128.6 (d), 128.5 (d), 128.2 (2d), 128.1 (d), 127.5 (d), 127.4 (2d), 127.0 (2d), 126.5 (d), 125.6 (2d), 123.5 (d), 60.1 (d), 33.6 (t); IR ν_{max} 3056, 1637, 1492, 1026, 700; HRMS for $C_{26}H_{18}Cl_2$: $M^{+}_{calcd.}$ 400.0780; M^{+}_{found} 400.0797.



endo,cis-**18**



endo,trans-**18**



endo-**19**

endo,cis-**18**: 10%; R_f 0.87 (petroleum ether/dichloromethane = 1:1); colourless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.37 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 8.5 Hz, 1H), 7.24–7.28 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.08 (td, J = 7.4; 0.9 Hz, 1H), 6.88 (td, J = 7.4; 0.9 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 6.61–6.67 (m, 1H), 6.42–6.46 (m, 1H), 6.28 (d, J = 11.8 Hz, 1H), 6.24 (d, J = 7.4 Hz, 1H), 5.44 (dd, J = 11.8; 9.8 Hz, 1H), 5.29–5.31 (m, 1H), 3.95–3.98 (m, 1H), 3.70 (d, J = 9.8 Hz, 1H), 3.20 (d, J = 5.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 150.0 (s), 139.6 (s), 139.3 (s), 135.5 (s), 134.7 (d), 134.5 (d), 132.1 (s), 131.6 (s), 129.5 (d), 129.5 (d), 129.3 (2d), 128.0 (d), 127.8 (d), 127.4 (2d), 127.4 (d), 126.7 (d), 126.2 (d), 125.9 (d), 125.1 (d), 120.9 (d), 54.1 (d), 53.7 (d), 46.2 (d), 45.8 (d); IR ν_{max} 3022, 1670, 1490, 1092, 1014, 735; HRMS for $C_{26}H_{20}Cl_2$: $M^{+}_{calcd.}$ 402.0937; M^{+}_{found} 402.0921.

endo,trans-**18**: 50%; R_f 0.87 (petroleum ether/dichloromethane = 1:1); colourless crystals; mp 151 °C; UV (96% EtOH) λ_{max} (log ε) 262 (4.35), 291 (3.42), 302 (3.14); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.10–7.20 (m, 7H), 7.07 (td, J = 7.4; 0.8 Hz, 1H), 6.87 (td, J = 7.4; 0.8 Hz, 1H), 6.65 (d, J = 8.3 Hz, 2H), 6.44 (d, J = 15.9 Hz, 1H), 6.42–6.46 (m, 1H, H_A), 6.22 (d, J = 7.3 Hz, 1H), 5.31 (ddd, J = 9.4; 3.5; 1.7 Hz, 1H, H_B), 4.00–4.03 (m, 1H), 3.39 (d, J = 8.4 Hz, 1H), 3.25 (d, J = 4.7 Hz, 1H), 3.22 (d, J = 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 149.9 (s), 139.8 (s), 139.0 (s), 135.4 (s), 134.7 (d), 132.3 (d), 132.2 (s), 131.6 (s), 129.3 (2d), 128.8 (d), 128.0 (2d), 127.4 (2d), 126.8 (2d), 126.6 (d), 126.6 (d), 126.2 (d), 125.7 (d), 125.1 (d), 120.8 (d), 58.4 (d), 53.8 (d), 46.1 (d), 45.9 (d); IR ν_{max} 3024, 1648, 1490, 1091, 1014, 730; HRMS ($-H^{+}$) for $C_{26}H_{20}Cl_2$: $M^{+}_{calcd.}$ 401.0869; M^{+}_{found} 401.0860.

endo-**19**: 10%; R_f 0.81 (petroleum ether/dichloromethane = 1:1); colourless oil; UV (96% EtOH) λ_{max} (log ε) 262 (4.38), 291 (3.45), 302 (3.18); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.27 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 8.5 Hz, 2H), 7.07 (dt, J = 7.6; 0.8 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 6.89 (dt, J = 7.6; 0.8 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 7.6 Hz, 1H), 6.31 (d, J = 15.8 Hz, 1H), 5.38 (dd, J = 15.8; 8.0 Hz, 1H), 3.55 (dd, J = 4.6; 2.1 Hz, 1H), 3.23 (t, J = 4.6 Hz, 1H), 3.14–3.18 (m, 1H), 2.43 (t, J = 7.0 Hz, 1H), 1.97 (dt, J = 7.0; 2.1 Hz, 1H), 1.85 (dt, J = 7.0; 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 138.7 (s), 136.0 (s), 135.9 (s), 132.6 (s), 132.5 (s), 131.5 (s), 130.5 (d), 129.1 (d), 128.9 (2d), 128.4 (2d), 127.7 (2d), 127.2 (2d), 126.5 (d), 126.3 (d), 125.2 (d), 124.8 (d), 48.2 (d), 44.1 (d), 44.0 (d), 21.8 (d), 21.1 (d), 18.0 (d); IR ν_{max} 2920, 1640, 1488, 1091, 751; HRMS ($-H^{+}$) for $C_{26}H_{20}Cl_2$: $M^{+}_{calcd.}$ 401.0869; M^{+}_{found} 401.0851.

Single crystal measurement was performed on an Oxford Diffraction Xcalibur Nova R (microfocus Cu tube) at room temperature [293(2) K]. Program package CrysAlis PRO [35] was used for data reduction. The structure was solved using SHELXS97[36] and refined with SHELXL97 [36]. The model was refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to C atoms were modelled as riding entities using the AFIX command. Molecular geometry calculations were performed by PLATON [37], and molecular graphics were prepared using ORTEP-3 [34], and CCDC-Mercury [38]. Crystallographic and refinement data for the structures reported in this paper are shown in Table 1.

Supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223 336033; or deposit@ccdc.cam.ac.uk). CCDC-928402 contains the supplementary crystallographic data for this paper.

Acknowledgements

This work was supported by grants from the Ministry of Science, Education and Sports of the Republic of Croatia (Grant Nos. 125-0982933-2926, 098-0982929-2917, and 098-1191344-2943).

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