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Synthesis, Photochemistry, and Photophysics of Butadiene Derivatives: Influence of the Methyl Group on the Molecular Structure and Photoinduced Behavior[†]

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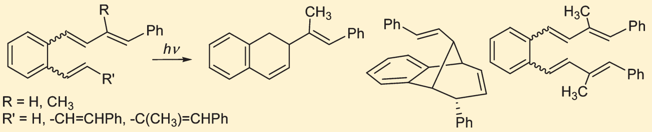

ABSTRACT: Novel butadiene derivatives display diverse photochemistry and photophysics. Excitation of 2-methyl-1-(*o*-vinylphenyl)-4-phenylbutadiene leads to the dihydronaphthalene derivative, whereas photolysis of the corresponding model *o*-methyl analogue results in the formation of the naphthalene-like derivative, deviating from the nonmethylated analogue of the prior starting compound and producing benzobi- and -tricyclic compounds. The effect of the methyl substituents is even more dramatic in the case of the dibutadienes. The parent unsubstituted compound undergoes photoinduced intramolecular cycloaddition giving benzobicyclo[3.2.1]octadiene, whereas the photochemical reaction of the corresponding 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. 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 together. Four molecules of very similar structures show dramatically different photoinduced behavior, revealing how changes of the nature and position of the substituents are valuable in understanding the photophysics and photochemistry of these types of compounds.

INTRODUCTION

The photochemistry of 1,3-butadiene[1] and 1,3,5-hexatriene[2] derivatives has been studied in detail. The photochemical reactions of 1,4-diphenyl-1,3-butadienes, their photoisomerization reactions,[3−11] and some electrocyclization reactions[12,13] have already been studied. However, the photochemistry of 1-(*o*-vinylphenyl)-4-phenylbutadiene derivative **1** (Figure 1) was described for the first time by our group.[14] The synthesis and photochemistry of **1**, a molecule that combines properties of both butadiene and hexatriene systems, were examined. Previous publications[15−22] on the photochemistry of different heteroaryl-substituted hexatrienes showed interesting intramolecular cycloaddition reactions and formation of bicyclo[3.2.1]octadiene structures. By insertion of an additional double bond into the stilbene-like moiety, we obtained the prolonged conjugated system of **1** that might allow the formation of a new polycyclic structure with the double bond functionality for further transformations. The compound **1** undergoes intramolecular photocycloaddition reaction to benzobicyclo[3.2.1]octadiene derivative **2** in very good yield, giving only the *endo*-phenyl-benzobicyclo[3.2.1]-octadiene isomer (*endo*-**2**) due to the stereoselectivity of the photoreaction. The phenyl-benzobicyclo[3.2.1]octadiene derivative (*endo*-**2**) undergoes further di-π-methane rearrangement leading to tricyclic structure (*endo*-**3**), or it can be used as a suitable substrate for other transformations on the isolated double bond, easily derivatized to new compounds with various functionalities. Moreover, the bicyclo[3.2.1]octane skeleton is found in numerous biologically important active natural products.[23−26]

As a part of our increasing interest in the photochemistry of conjugated butadiene systems, we extended our research to new ω,ω′-diarylbutadiene derivatives **4**−**7** (Figure 1) in order to prepare new polycyclic structures by photochemical methodology as well as to get a deeper understanding of the photoinduced behavior of these conjugated systems. In the continuation of our study of 1-(*o*-vinylphenyl)-4-phenylbutadienes **1**,[14] the synthesis of four novel butadiene derivatives **4**−**7** (unsubstituted or having one or two methyl groups as substituents on the double bond), their spectral characterization, and the detailed investigation of the photochemical and, to a less extent, photophysical behavior are presented. In these new systems with prolonged conjugation, the influence of the introduced methyl group at the double bond is examined in order to see the possibility of the intramolecular [2 + 2] photocycloaddition followed by formation of the

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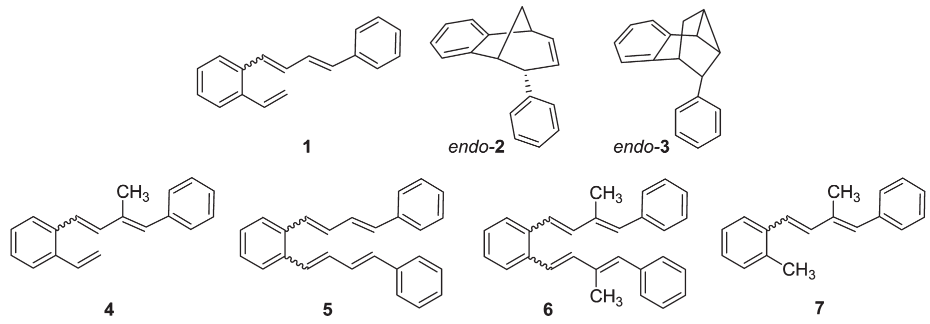
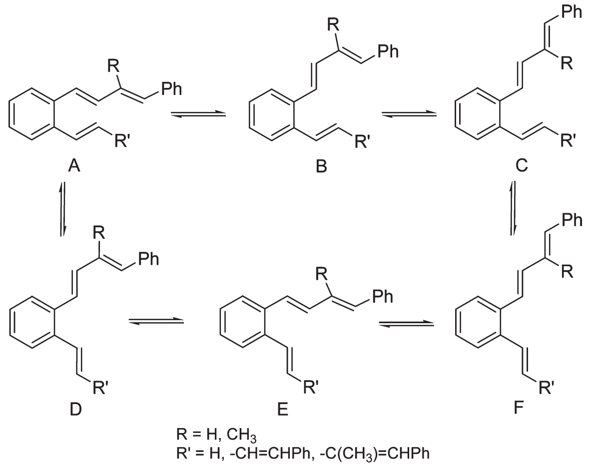


Figure 1. Structures of the known (**1**) and new butadiene derivatives (**4**−**7**) and photoproducts of **1** (**2** and **3**).

Scheme 1. Possible Conformations of *trans*-Isomers of Compounds 1 and 4−6

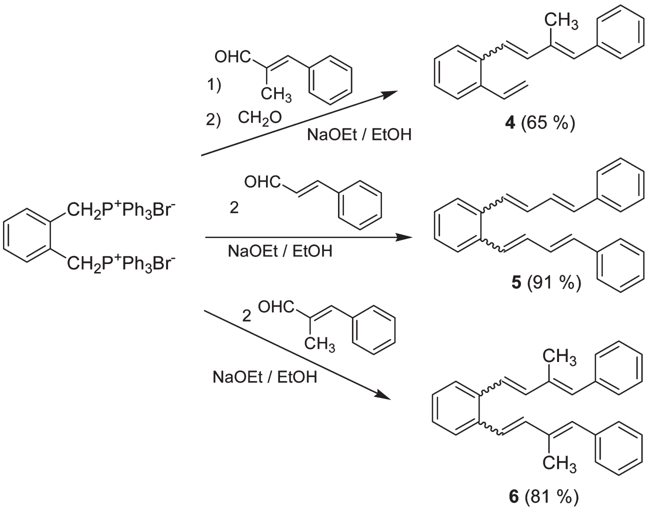


benzobicyclo[3.2.1]octadienes and/or photoelectrocyclization to the photoproducts possessing six-membered rings. The steric hindrance of the methyl groups in **4** and **6** should cause deviations from planarity[27] and should shift the conformer equilibrium toward *s-cis*-butadiene conformers, (e.g., B and D, Scheme 1), affecting the reaction pathways and yields. As only some of the conformers can react in the formation of intramolecular photoproducts, it is not expected that the photoreactions take place always from the most populated conformer (e.g., D for compound **4** and **6**, Scheme 1) regardless of the conformational distribution of the starting molecule. In the case of **1**,[14] the same conformer B was responsible for the formation of **2** at different wavelengths; even various conformers exist mainly at different reaction conditions. Although the conformers of each isomer studied in this work may display deviating photoinduced behavior, similarly to some 2-vinylbiphenyls,[28] 1,2-dinaphthylethenes,[29] and 1-naphthyl-2-phenylethenes,[30] investigation of the effects of the conformational diversity within the steric influence of the starting geometric isomers on the reaction pathway was not our aim.

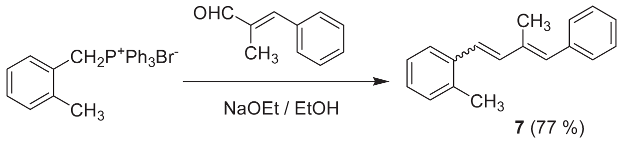
RESULTS AND DISCUSSION

The starting materials, unsubstituted (**5**) and methyl-substituted butadiene derivatives (**4**, **6**, and **7**), were prepared by the Wittig reaction from the corresponding mono- or diphosphonium salts and cinnamaldehydes (Schemes 2 and 3) in very good yields (65−91%) as mixtures of two (compounds **4** and **7**) or three geometric isomers (compounds **5** and **6**) according to the procedures described in previous papers for heteroarylstilbene derivatives[31,32] and butadiene analogues.[14] Because the syntheses were performed always from the corresponding (*E*) geometric isomer of the cinnamaldehydes, the second double bond (looking from the *ortho*-substituted central benzene ring) in the starting compounds **4**−**7** retain the (*E*) configuration. Hence, the number of the geometric isomers was reduced; the reaction mixtures contain *cis*- and *trans*-isomers of **4** and **7** and *cis,cis*-, *cis,trans*-, and *trans,trans*-isomers of **5** and **6** (only the first double bond connected to the *ortho*-substituted central benzene ring is designated).

Scheme 2. Syntheses of New Butadiene Derivatives 4−6 by Wittig Reaction



Scheme 3. Synthesis of New Butadiene Derivative 7 by Wittig Reaction



To confirm that the vinyl group in **4** is involved in the photoreaction and to resolve geometric isomers of starting compound **4**, the *o*-methyl-substituted derivative **7** was irradiated as the model of an *o*-vinyl-substituted conjugated system **4**

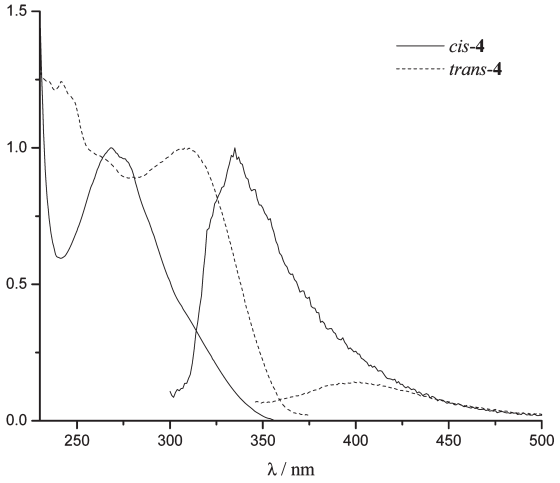


Figure 2. Absorption and emission spectra of the isomers of compound **4**.

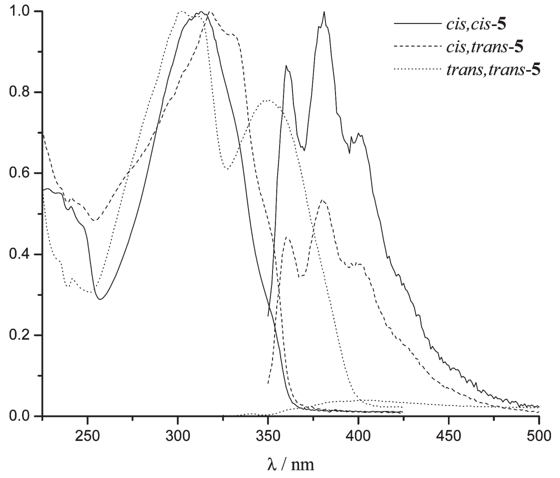


Figure 3. Absorption and emission spectra of the isomers of compound **5**.

without a possibility of intramolecular photoreaction and polymerization due to the lack of the vinyl group.

The geometric isomers of **4**−**7** can be easily identified according to 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 **4** and **7** was very similar (∼1:3), whereas the ratio of *cis,cis*-, *cis,trans*-, and *trans,trans*-isomers of **5** and **6** was ∼1:5:4). The isomers of **4**−**7** were separated by combining column and thin-layer chromatography on silica gel, completely analyzed, and identified spectroscopically.

UV Absorption Spectra. The UV spectra (Figures 2, 3, 4, and 5) of separated isomers of **4**−**7** clearly show the substituent and configurational influence on absorption characteristics. Table 1 summarizes the characteristic data (maxima wavelengths and vibronic progression of the absorption and emission spectra, the fluorescence quantum yields and lifetimes) of the compounds studied in *n*-hexane.

The positions and intensities of the absorption bands indicate that the increasing participation of the *trans* configuration in the double bond causes a bathochromic shift and generally an increase in the molar absorption coefficients compared to the bands of the corresponding *cis*-isomers. This phenomenon can be attributed to the increased molecular planarity and the possibility of better delocalization of π electrons. Accordingly, in the case of compounds **4**, the main band of the *trans*-isomer (315 nm) is about 36 nm red-shifted compared to that of the *cis*-isomer (279 nm). Notably, the main bands of the isomers of this methyl-substituted butadiene derivative are significantly (about 25−30 nm) blue-shifted in comparison to those of the corresponding isomers of the unsubstituted analogue **1**.[14] The same relation is valid to the corresponding isomers of the 1,4-diphenyl-1,3-butadiene (DPB).[33] This indicates that the methyl group decreases the conjugation in the bond structure, significantly changing the geometry of the molecule[27,34] and influencing its conformational equilibrium and photoinduced behavior. The absorption spectrum of the *trans*-isomer of compound 7 is quite similar to that of the corresponding derivative **4**. Both the positions and the molar absorbances of the main band agree well, indicating that the change of the substituent (methyl vs vinyl) does not influence the S_0−S_1 transition assigned to this band. The first excited state of both compounds is delocalized over both the butadiene backbone and the phenyl groups.[27] Since neither the methyl nor the vinyl group on the aromatic ring affects the absorption spectrum of these butadiene derivatives, apparently these substituents do not influence the conjugation.

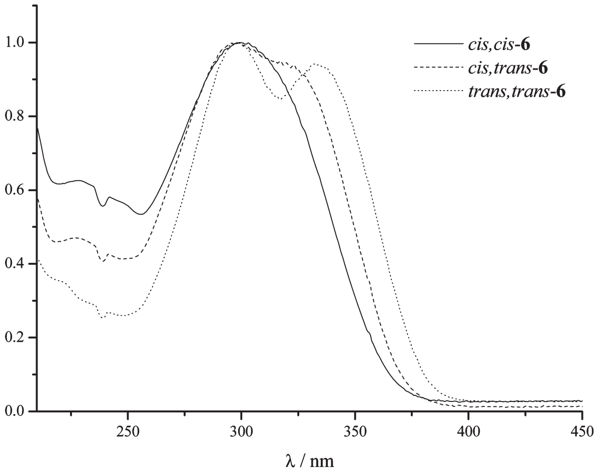


Figure 4. Absorption spectra of the isomers of compound **6**.

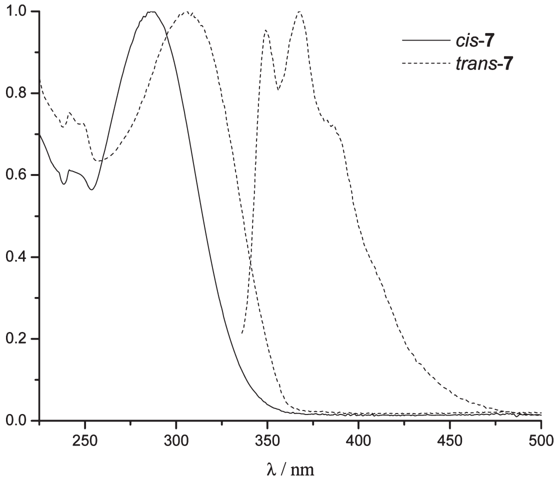


Figure 5. Absorption and emission spectra of the isomers of compound **7**.

Table 1. Absorption and Emission Parameters of Butadiene Derivatives in *n*-Hexane at Room Temperature

compound	λ_{abs}^{max}, nm[a]	$\Delta\tilde{\nu}_{abs}$, cm^{-1}	λ_{F}^{max}, nm	$\Delta\tilde{\nu}_{F}$, cm^{-1}	Φ_F[b] (λ_{exc}, nm)	τ_F, ns[c]
cis-**4**	271, $\underline{279}$ (4.13)		$\underline{335}$		0.021 (280)	5.97
trans-**4**	$\underline{315}$ (4.47)		$\underline{399}$		~0.003 (300)	2.54
cis,cis-**5**	$\underline{313}$ (3.83)		360, $\underline{381}$, 400	1530	0.246 (280)	0.52
cis,trans-**5**	$\underline{318}$ (4.48), 331, 353^{sh}	3120	360, $\underline{380}$, 399	1460	0.135 (280)	0.49
trans,trans-**5**	$\underline{303}$ (4.37), 312, 349^{sh}	4350	$\underline{406}$		0.017 (330)	0.21
cis,cis-**6**	$\underline{299}$ (4.49)				<0.001	~0.1
cis,trans-**6**	$\underline{291}$ (4.09), 326^{sh}	3690			<0.001	~0.1
trans,trans-**6**	$\underline{298}$ (4.43), 331^{sh}	3350			<0.001	~0.1
cis-**7**	$\underline{289}$ (4.34)				<0.001	nm[d]
trans-**7**	$\underline{312}$ (4.47)		349, $\underline{368}$, 384	1480	0.021 (297)	1.09

[a] The main maximum is underlined. [b] Standard deviation: ±5%. [c] ±4%. [d] Not measurable.

However, the second, higher-energy (240−260 nm) bands of the *trans*-isomers of **4** and **7** are significantly different. Since the corresponding second excited state is localized on just the phenyl moieties,[35] these substituents significantly affect its energy and the intensity of the S_0−S_2 transition (Figures 2 and 5).

The bathochromic effect of the *trans* configurations is more significantly manifested in the case of the dibutadiene derivatives **5** and **6** (Figures 3 and 4). While the *cis,cis*-isomers display one (merged) band assigned to the S_0−S_1 transition, in the spectra of the *cis,trans*- and especially of the *trans,trans*-isomers the low energy absorption splits into two bands. This phenomenon confirms that *trans* configuration increases the extent of conjugation and planarity of the molecule. The blue-shifts of the corresponding bands in the spectra of the derivatives **6** compared to those of the isomers of **5** are also in accordance with the effects of the methyl group on the butadiene backbones, reducing the conjugation and the planarity of the former compounds. Since, apart from the butadienes, no further substituents are on the phenyl groups, the position of the second, higher-energy (230−241 nm) band is almost constant for these compounds, and only its intensity is changed by the isomerization.

Fluorescence Emission Spectra and Photophysics. In *n*-hexane at room temperature these butadiene derivatives display diverse emission features strongly depending on their structures. The fluorescence spectrum of *cis*-**4** is characterized with a strong band at the shortest wavelengths (335 nm) among the emission bands of these compounds. At the same time, the fluorescence lifetime of this derivative is the longest one (Table 1). The low quantum yield indicates that fluorescence is not the main decay route of the S_1 excited state of this compound. In the case of the *trans*-isomer of **4** the efficiency of fluorescence is even weaker (about 1 order of magnitude). In the case of derivatives **7**, deviating from the compounds **4**, the *trans*-isomer displays a characteristic fluorescence with a low efficiency (0.02) and a relatively short lifetime (1.1 ns), whereas no emission could be detected for the *cis*-isomer under these circumstances. This phenomenon suggests that the substituent on the phenyl group (vinyl for **4** and methyl for **7**) strongly influences the emission properties, whereas it just slightly affects the absorption features related to the first excited state. In the case of derivatives **4**, the vinyl substituent decreases the fluorescence efficiency in the *trans* configuration. From derivatives **7** (with methyl substituent on the phenyl group) the *trans*-isomer displays appreciable fluorescence, whereas the emission of the *cis*-isomer is hardly detectable. This observation indicates that the excited singlet state of the latter species decays via nonradiative processes, such as IC and ISC. A similar phenomenon was observed in the case of DPB,[11,36] suggesting that the methyl substituent on the phenyl group barely affects the fluorescence properties of the diphenyl-butadiene derivatives. This conclusion is confirmed by the fact that the emission band of *trans*-**7** displays a vibronic fine structure, which agrees well with that of the *trans,trans*-DPB.[7,27,37] The strong deviation of the emission spectral properties of derivatives **4** (and also **5** as seen later) from those of **7** and DPB,[7,11] i.e., the \reversed tendency regarding the features of the *trans*- and *cis*-isomers, is rather surprising and may be attributed to the role of conformers and fast photoisomerization as one of our reviewers suggested. Thus, a reasonable explanation of such observations is that at the excitation wavelengths employed weakly fluorescent conformers of *trans*-**4** (and also *trans,trans*-**5**) were excited, but excitation of the *cis*-isomers led to adiabatic formation of strongly fluorescent conformers of *trans*-**4** (and *trans,trans*-**5**). Relevant precedents of such phenomena were observed for *cis*-1-(2-naphthyl)-2-phenylethene[38] and *cis*-1-(2-anthryl)-2-phenylethene[39] and systematically analyzed for various diarylalkenes.[40]

From the viewpoint of emission, the most interesting phenomenon can be observed in the case of the dibutadiene derivatives **5** and **6**. From isomers of **5**, which do not contain any substituent on either the butadiene backbones or the phenyl rings, the *cis,cis*-isomer efficiently fluoresces (Φ_F = 0.246), and its emission spectrum is characterized by a well resolved vibronic fine structure (Figure 3) (Table 1). The fluorescence of the *cis,trans*-isomer is very similar, but its quantum yield is 45% lower (Φ_F = 0.135). However, *trans,trans*-**5** displays an order of magnitude weaker (Φ_F = 0.017) and rather structureless emission. This tendency suggests that the all-*trans* configuration is not favorable for emission from the first excited state, and the main routes of the relaxation of the excited molecule are photochemical and internal conversion processes. Accordingly, the measured emission lifetime is the shortest one in this case (0.2 ns). Considering the values of the quantum yield and the vibronic fine structure of the fluorescence of *cis,cis*-**5** and *cis,trans*-**5**, it is clearly seen that the intensity (efficiency) of the characteristic fluorescence of the fine-structured spectrum is in direct proportion with the degree of *cis* configuration in these molecules. The tendency regarding the emission spectral properties of the derivatives **5**, similarly to those of the isomers **4**, is just the reverse for that observed for **7** and DPB.[7,11] A reasonable explanation for this phenomenon is previously given in the discussion of the fluorescence features of the derivatives **4**. Nevertheless, the double butadiene structure of **5** may also play a considerable role in this photophysical behavior strongly deviating from that of the parent compound (DPB).

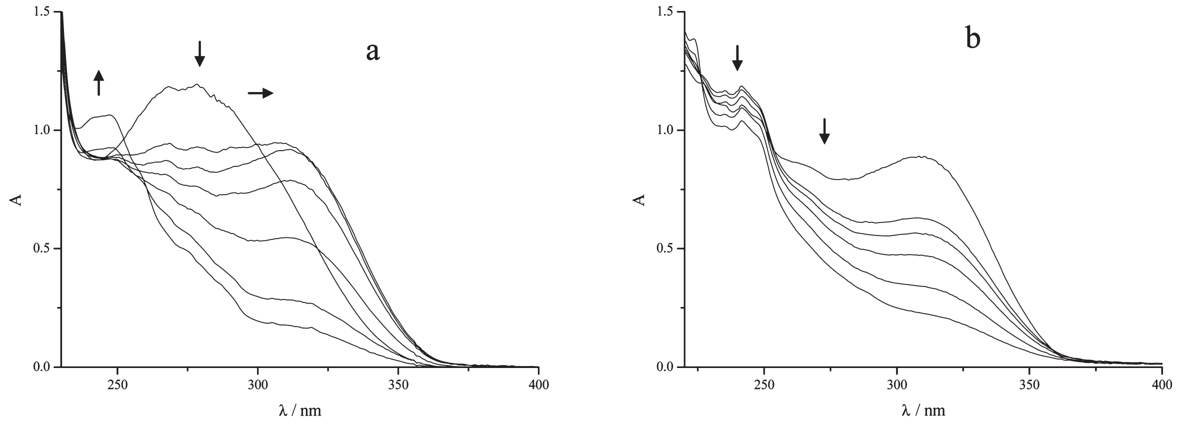


Figure 6. Spectral change during the irradiation of *cis*-**4** in *n*-hexane (a) after 0, 10, 20, 40, 80, 160, 320 s; and *trans*-**4** in *n*-hexane (b) after 0, 10, 20, 40, 80, 160 s (λ_{ir} = 313 nm, *l* = 1 cm).

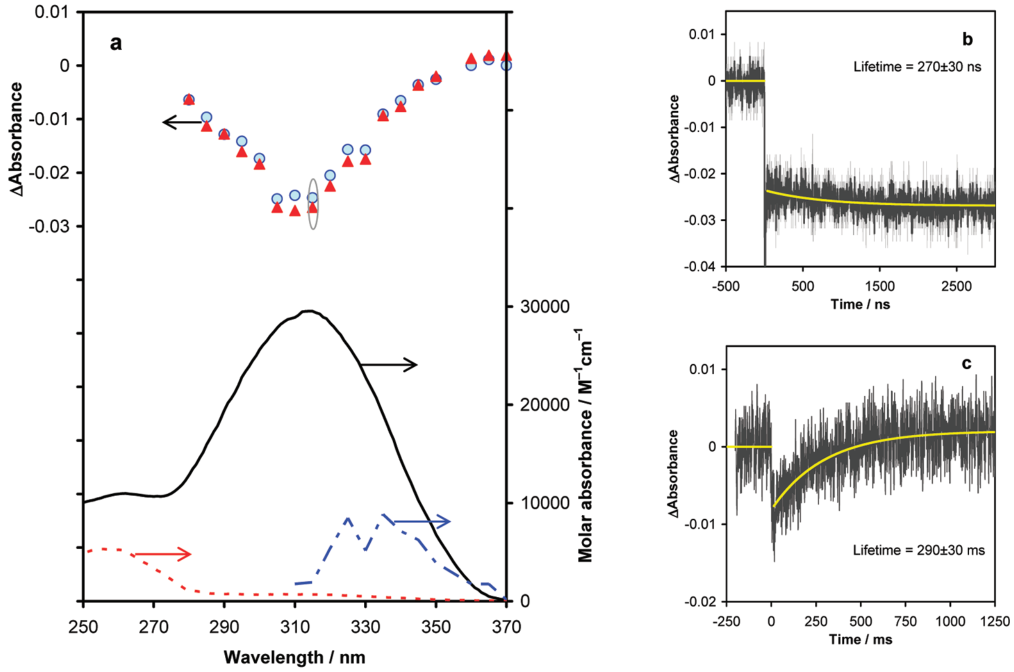


Figure 7. Transient absorption spectra of *trans*-**4** recorded at 100 (●) and 3000 ns (▲) after the excitation and the estimated spectrum of the short-lived intermediate (dash-dot line) along with the spectrum of the starting material (solid line) and that of the final product (dashed line) (a). The decay curves at 315 nm in shorter (b) and longer (c) time scale are also displayed.

Methyl substituents on the butadiene backbones of dibutadiene derivative **6** result in dramatic change in the emission. Although due to the high sensitivity of our equipment extremely weak ($\Phi < 0.001$) structureless fluorescences were detected for these compounds at longer wavelengths (not shown in Figure 4) with rather short lifetimes (about 0.1 ns), these emissions can be considered negligible compared to those of derivatives **5**. This may be attributed to the strong steric crowding as a mutual effect of the phenyl and methyl groups, besides the reduction of the extent of conjugation. This steric strain may cause the lack of planarity even in the case of *trans*,*trans*-**6** and the twisting of the two terminal phenyl groups around the butadiene backbones. A similar phenomenon was observed for the sterically hindered tetraphenylmethylbutadiene (TPMB).[27]

Photochemistry. Irradiation experiments with each isomer of **4**–**7** were carried out in *n*-hexane, and the reaction course was followed by taking the UV spectra at indicated times. These experiments were performed to study the effect of the configuration and the methyl substituents on the route of the photolysis. The systems were argon-saturated to avoid the photoinduced oxidation of the excited molecules. The concentration of the starting compounds was on the order of 10^{-4} M. The excitation wavelengths of 313 and 350 nm were applied for each photolysis experiment. The preparative irradiation experiments of **4**–**6** were performed in petroleum ether solutions under anaerobic conditions at 313 and 350 nm and at low concentrations in the order of 10^{-3} M. Depending on the starting material, different photochemical routes and, as a consequence, different types of photoproducts were identifed and confirmed. The formation of the photoproducts was generally accompanied by the formation of some polymeric products, which were not further investigated.

Regardless of the derivative, upon irradiation of each isomer the longest-wavelength absorption band gradually disappeared (see Figures 6, 9, 12, and 16 for 313 nm photolysis; the spectral changes at 350 nm irradiation (not shown) are very similar to the corresponding ones at λ_{ir} = 313 nm). These spectral changes indicate that the long-range conjugation between the phenyl groups via the butadiene link has been ceased by the photolysis, and the electronic system of the aromatic rings became isolated. In numerous cases, as the initial changes of the absorption spectra indicate (Figures 6a, 9b, 12ab, 16a), photoisomerization is one of the primary process, which is either followed or accompanied by a competitive photochemical reaction.[41,42] Hence, in these cases, the quantum yield for the disappearance has been determined from the spectra recorded after the quasi-photostationary state of the isomers was reached. This took place very fast, within 20 s of irradiation. The initial slope (at t = 0 s) of the polynom fitted to the absorbance vs time plot at the most characteristic wavelength has been taken for the calculation of the quantum yield. Also the molar absorbance of the final product at this wavelength was taken into account. The quantum yields of the photoinduced disappearance determined in this way are summarized in Table 2.

As Figure 6a shows, in the initial period of irradiation of *cis*-**4** an efficient photoisomerization to *trans*-**4** takes place (in accordance with the interpretation of the surprising fluorescence properties of isomers **4**), which is followed by a gradual disappearance of the longer-wavelength band, while a moderate increase of the shorter-wavelength band (below 250 nm) can be observed (Figure 6a). The latter suggests the increase of the absorption assigned to the phenyl ring independently of the butadiene backbone. In the case of the *trans*-**4** as starting material, no isomerization can be observed on the basis of the spectral change, only the gradual disappearance of the longer-wavelength band accompanied by a slight decrease of the absorption band at higher energies. The quantum yield of the disappearance at 313 nm irradiation is quite high (0.75) for *cis*-**4**, whereas it is significantly lower, although still appreciable, for *trans*-**4** (0.31). The corresponding quantum yields at λ_{ir} = 350 nm are similar but somewhat lower (0.29 and 0.22). Since only the *cis*-isomer displays inclination to thermal electrocyclization as quite recently observed,[43,44] such a reaction may significantly contribute to the higher quantum yield for *cis*-**4**. Also polymerization can occur in the case of **4**, due to the vinyl substituent. Since the fluorescence quantum yields of these derivatives are about 2 orders of magnitude lower than those of the photochemical disappearance, emission from the S_1 excited state does not efficiently compete with the latter process in these cases. The sum of the quantum yields regarding the fluorescence and the photochemical disappearance is significantly lower than unity, especially in the case of

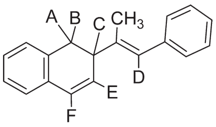


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Figure 8. Structure of photoproduct **8** with proton assignments (A−F).

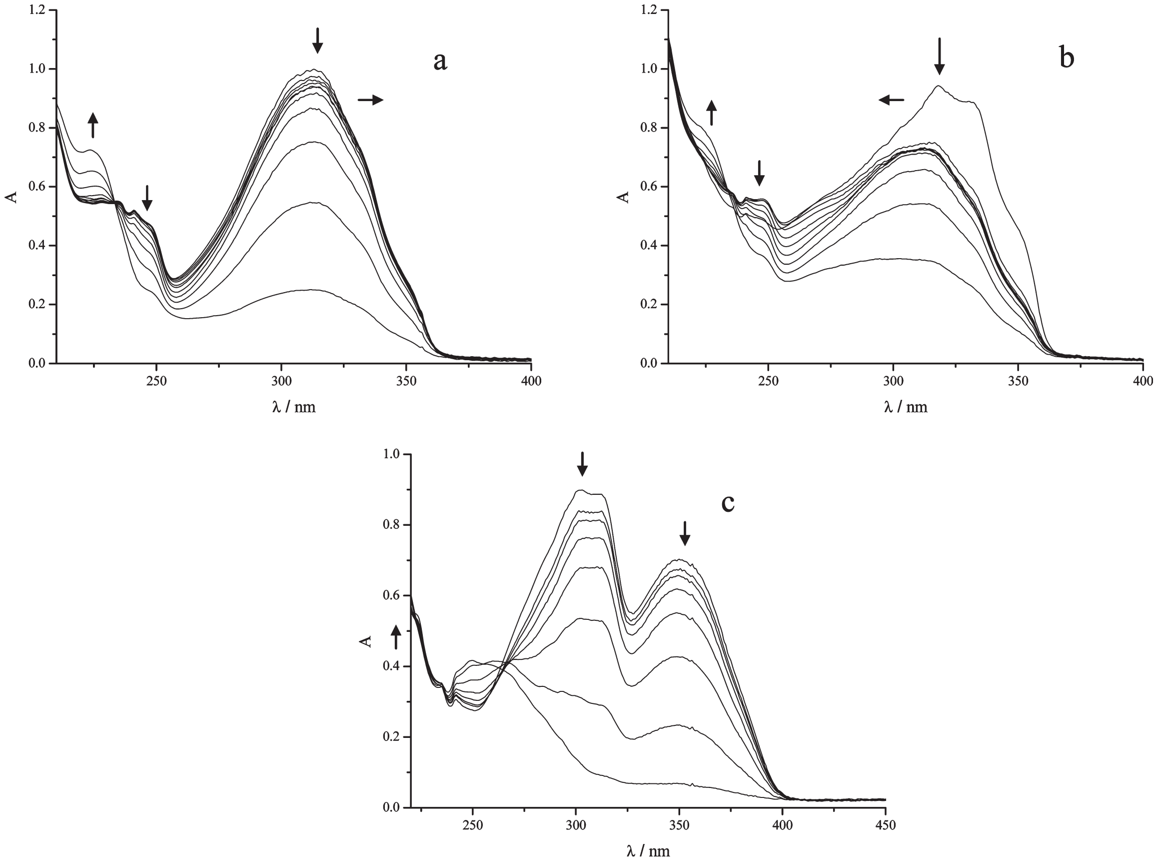


Figure 9. Spectral change during the irradiation of (a) *cis,cis*-**5** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, 5120 s; (b) *cis,trans*-**5** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280, 2560 s; and (c) *trans,trans*-**5** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640 s (λ_{ir} = 313 nm, l = 1 cm).

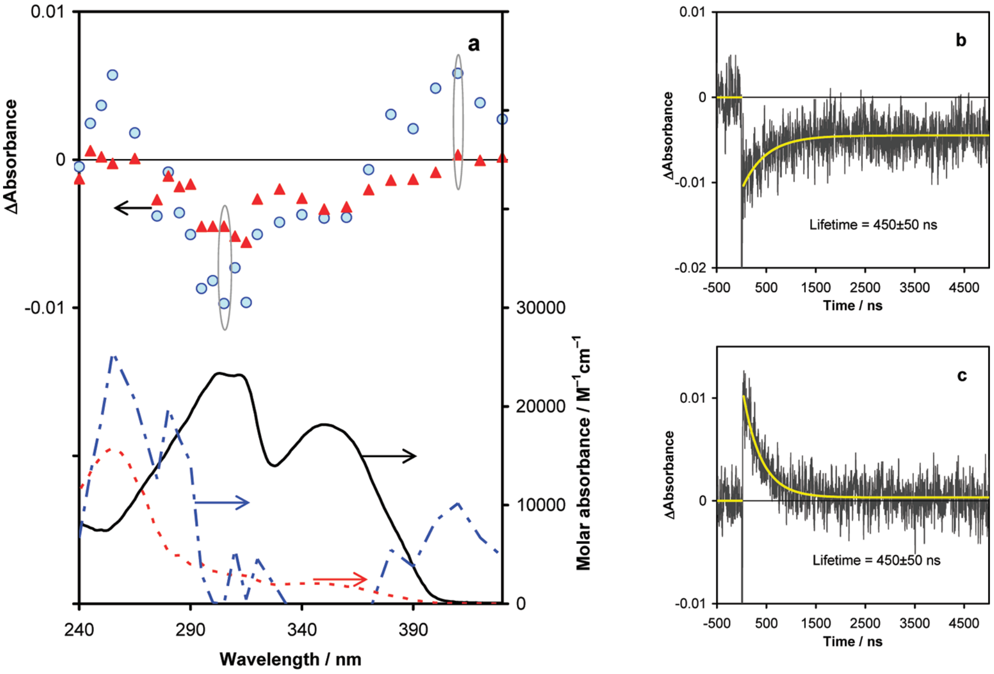


Figure 10. Transient absorption spectrum of *trans,trans*-**5** recorded at 150 (●) and 3000 ns (▲) after the excitation and the estimated spectrum of the intermediate (dash-dot line) along with the spectrum of the starting material (solid line) and that of the final product (dashed line) (a). The decay curves at 305 nm (b) and 400 nm (c) are also displayed.

the *trans*-isomer, indicating that other processes, such as internal conversion (IC), may play important role as decay channels of the excited-state molecule. A similar phenomenon was recently observed for the *trans,trans*-isomer of DPB.[45]

Time-resolved absorption measurements gave some hints regarding the photochemical decay routes of the excited states. Although all derivatives in this study were investigated by laser flash photolysis, only the all-*trans*-isomers gave appreciable signals, similarly to the observations on 1,4-diphenylbutadienes.[11] Flash photolysis experiments with *trans*-**4** resulted in significant transient absorption changes, mostly bleaching in the wavelength range of the starting compound (Figure 7). Because of the strong absorption of the initial derivative, the estimation of the transient absorption spectrum (see in the Experimental Section) is very uncertain. It shows a band at 320−350 nm (Figure 7a), and its lifetime is 270 ± 20 ns (Figure 7b). This transient might be attributed to the formation and decay of the triplet excited state of *trans*-**4**; however, according to the previous studies on the parent compound (DPB), the intersystem crossing in that case is very inefficient.[4,11]

The triplet state of DBP in solution displayed a wide band (in the range of 360−420 nm) centered at about 390 nm,[11] and its lifetime was determined to be 1.6 μs.[4,11] On the basis of the absorption band, the transient in our work (Figure 7a) may be assigned to the triplet state, but its lifetime is much shorter than that observed for the triplet state of its parent compound. The fluorescence efficiencies of the isomers of **4** are rather low (0.021 and 0.003 for the *cis*- and *trans*-isomers, respectively), whereas the quantum yields of their photochemical disappearance are appreciably high (0.75 and 0.31 at λ_{ir} = 313 nm, 0.29 and 0.22 at λ_{ir} = 350 nm), indicating that the singlet excited state much more efficiently decays via chemical conversion than through radiative pathways. Since on the basis of the observations regarding DPB the triplet formation without appropriate sensitizer is not favorable and it has a relatively long lifetime (1.6 μs),[4,11] the short-lived transient observed for *trans*-**4** may be assigned to a radical intermediate. This short-lived species decays to form a long-lived one with a lifetime of 290 ± 30 ms. Its molar absorbance at 310 nm is lower than that of the former intermediate, as seen in Figure 7c. Also this long-lived species may be a biradical, as shown later in Scheme 3.

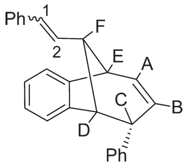


Figure 11. Structure of photoproduct *exo,endo*-**13** with proton assignments (A−F).

On preparative irradiation of 2-methyl-1-(*o*-vinylphenyl)-4-phenylbutadiene derivative (**4**) at 350 nm, cyclohexadiene derivative **8** was found and isolated as the main photoproduct as a result of an electrocyclic ring-closure process characteristic for 1,3,5-hexatriene (Scheme 3).[3,46] The proposed reaction mechanism for transformation of the *o*-vinyl derivative **4** involves a six-membered ring closure followed by a sigmatropic 1,5-H shift to give **8**. A primary photochemical process observed after very short irradiation time is *cis*−*trans* isomerization giving preferably the *trans*-**4** isomer (existing in different conformations; Scheme 1 and 4) followed by competitive processes from two different conformations of *trans*-**4** (Scheme 4).

After the complete conversion from the favored conformation, the main photoproduct **8** was obtained with the yield of 52% at 350 nm and less selectively with 34% yield at 313 nm and separated by column chromatography on silica gel, and its structure was deduced unequivocally from spectral studies. In

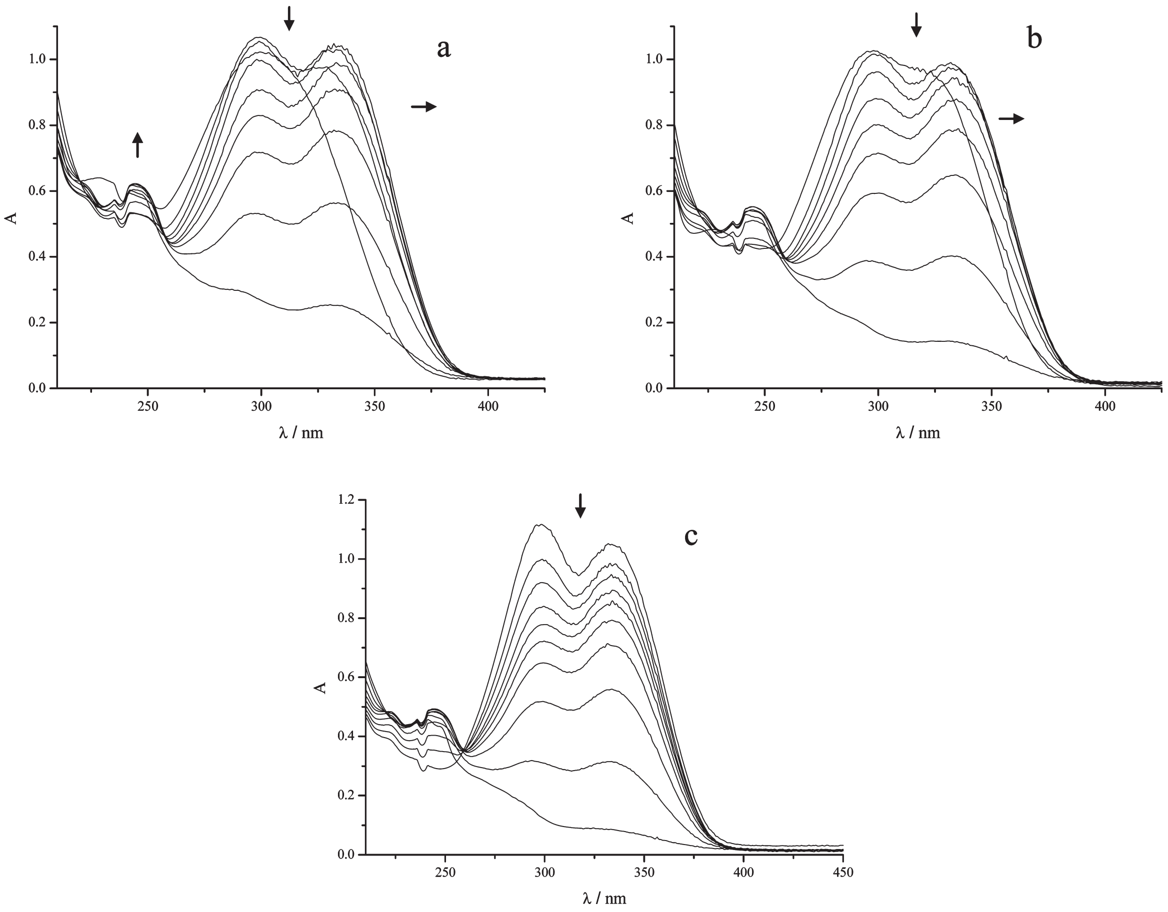


Figure 12. Spectral change during the irradiation of (a) *cis,cis*-**6** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280 s; (b) *cis,trans*-**6** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280 s; and (c) *trans,trans*-**6** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280, 2560 s (λ_{ir} = 313 nm, l = 1 cm).

the last fractions minor product **9**, 7-methyl-6-phenyl-6,9-dihydro-5*H*-5,9-methano-benzocycloheptene, was isolated in traces at 350 nm but in 11% yield at 313 nm. Irradiation at 313 nm excites also the conformer that leads to **8**, but less intensively than the 350 nm irradiation. It is obvious that the 350 nm excitation excites more intensively the other conformer than the shorter wavelength favoring the formation of minor product **9**.

From the ^{1}H and ^{13}C NMR spectra of **8**, using different techniques (COSY, NOESY, HSQC, and HMBC), all protons and carbons were completely assigned. As it can be seen from the structure (Figure 8) the photoproduct **8** contains one pair of geminal protons (A and B), allyl proton C, and vinyl proton D, which occur in the ^{1}H NMR spectrum between 3.5 and 3.7 and 4.4−4.9 ppm, respectively. Its ^{13}C NMR spectrum shows four singlets, 11 aromatic and 1 aliphatic doublet, 1 triplet, and 1 quartet. Additionally, the MS spectra were very informative. The main photoproduct **8** had the same molecular ion m/z 246 as the starting compound **4**. The byproduct **9** in the photoreaction of **4** had also molecular ion m/z 246 and was formed as a result of intramolecular cycloaddition process from the other conformation of *trans*-**4** (Scheme 4).

Minor quantities of byproduct **9**, having benzobicyclo[3.2.1]octadiene structure, were formed by initial intramolecular cycloaddition and formation of resonance-stabilized intermediate **10**, followed by 1,6-ring closure and rearomatization (Scheme 4). Product **9** was seen in enriched chromatographic fractions and was identified according to the very well resolved four-proton pattern in the ^{1}H NMR spectrum and by the characteristic couplings for this type of rigid bicyclo[3.2.1]octadienes as published by us earlier in the photochemical reactions of β-heteroaryl-substituted *o*-divinylbenzenes[15−18] and unsubstituted butadiene derivatives.[14] It might be assumed that even if the 1,4-ring closure[41] to benzobicyclo[2.1.1]hexene derivative **11** is also operating from **10**, the formed derivative **11** could thermaly reverse to **10** and subsequently give the more stable product **9**. Possible photoproduct **12** (Scheme 4) having benzobicyclo[3.1.0]hexene structure has not formed.

Regarding the mechanistic considerations, the formation of the six-membered ring in **8** is obviously preferable and more plausible due to the steric hindrance of the methyl group[27] in comparison with the photochemistry of unsubstituted derivative **1** giving benzobicyclic structure **2** as the only photoproduct (Figure 1). The initial intramolecular photocycloaddition leading to the bicyclic structure **9** is a less favorable process, while the initial 6π electrocyclization leading to **8** is the dominant one. We assume that due to the dramatic changes induced by the steric effect of the methyl group in the excited state of *trans*-**4** the resonance through the nonplanar part of the molecule, which contains the methyl group, is generally not favorable (especially at 350 nm) even if it is formed from the more preferred conformer of *trans*-**4**.

In an effort to study the influence of prolonged conjugation in our systems on the course of the photoreaction, we introduced in

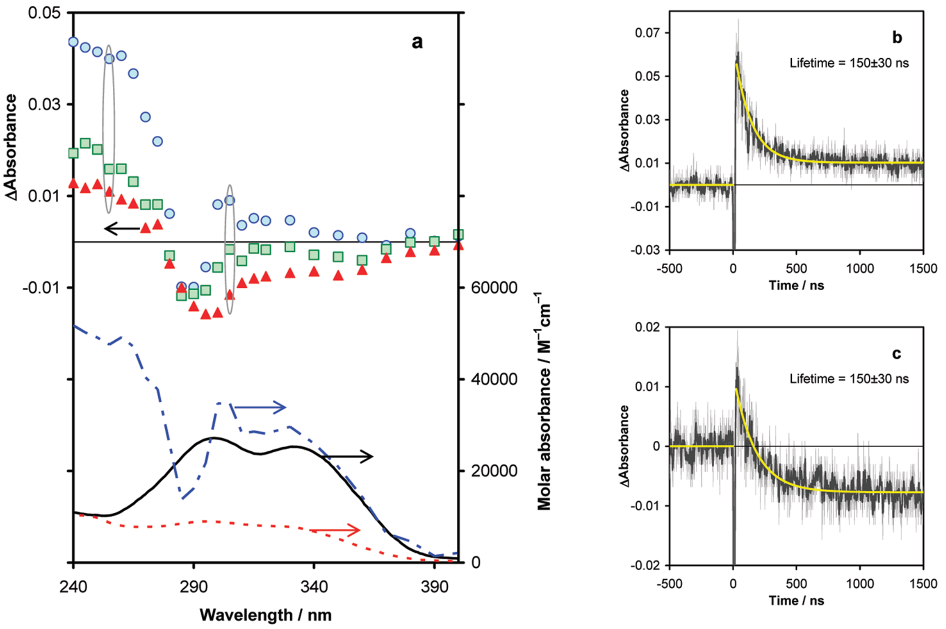


Figure 13. Transient absorption spectra of *trans,trans*-**6** recorded at 80 (●), 150 (■), and 6000 ns (▲) after the excitation and the estimated spectrum of the short-lived intermediate (dash-dot line) along with the spectrum of the starting material (solid line) and that of the final product (dashed line) (a). The decay curves at 255 nm (b) and 310 nm (c) are also displayed.

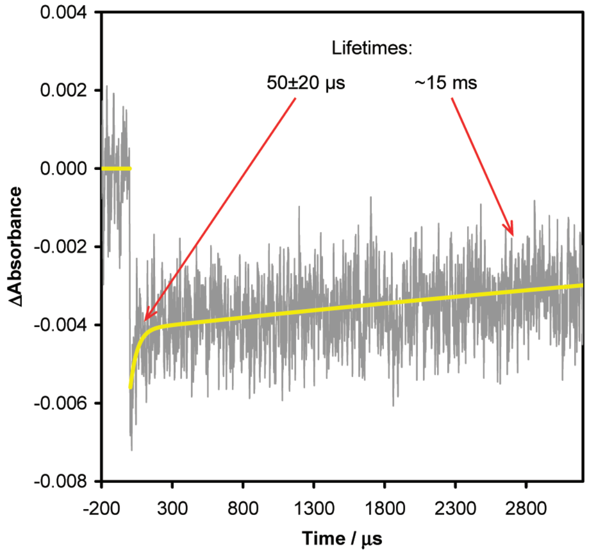
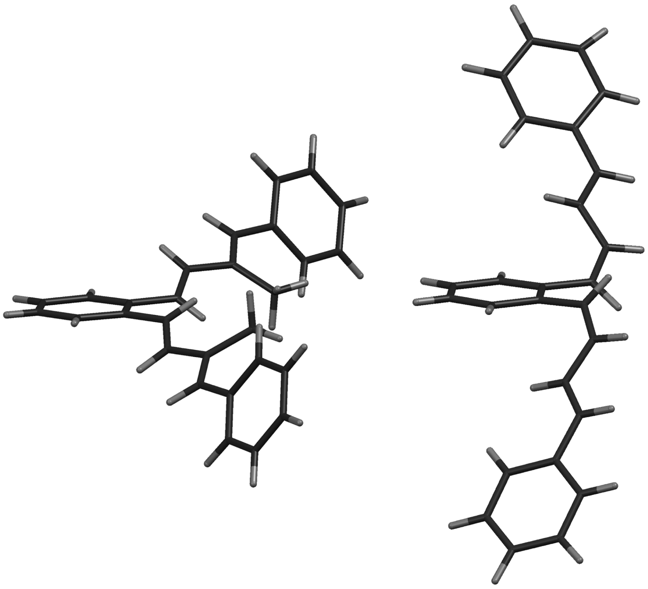


Figure 14. Two-stage (biexponential) transient absorption signal (decay curve) of *trans,trans*-**6** at 300 nm on a longer time scale.

the compound **1** a second styryl substituent at the β-position of the vinyl group, gaining new dibutadiene derivative **5**. Photolyses of these isomers display different characteristics at the initial period of irradiation, depending on the type of the starting isomer. Whereas in the case of *cis,trans*-**5** an efficient photoisomerization to *cis,cis*-**5** can be observed (Figure 9b), no spectral change indicates the geometrical isomerization of either the *cis,cis*-**5** (Figure 9a) or the *trans,trans*-**5** (Figure 9c) derivative. This phenomenon suggests that the 313 and also 350 nm excitation does not promote efficient isomerization of *trans,trans*-**5** through *cis,trans*-**5** to *cis,cis*-**5**, probably due to the too high activation barrier between the *trans,trans* and *cis,trans* geometries.



a) b)

Figure 15. Molecular structure of (a) *trans,trans*-**6** and (b) *cis,cis*-**5**. While the central *o*-dimethine moiety is less strained in the *cis,cis* configuration, due to the presence of methyl groups in **6**, the overall steric strain is smaller for *trans,trans*-isomer.

Surprisingly, however, the fluorescence spectra in Figure 3 indicate efficient adiabatic photoisomerization of *cis,cis*-**5** to *trans,trans*-**5**. The spectral change at longer irradiation times indicates disruption of the long-range conjugation and the increased part of the structural elements absorbing at shorter wavelengths. The quantum yields of the photoinduced disappearance at λ_{ir} = 313 nm are relatively low for the *cis,cis*- and *cis,trans*-isomers, Φ = 0.14 and 0.11, respectively. These similar values of

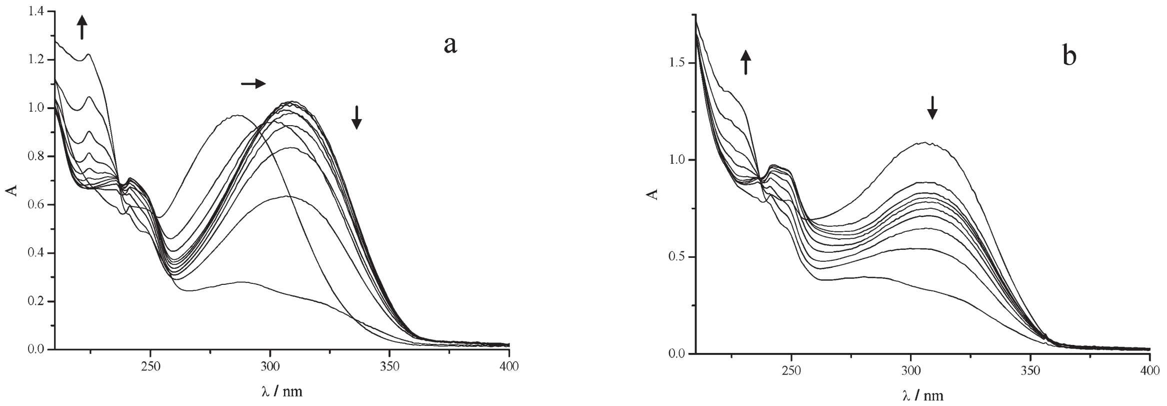


Figure 16. Spectral change during the irradiation of (a) *cis*-**7** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, 5120 s; and (b) *trans*-**7** in *n*-hexane after 0, 10, 20, 40, 80, 160, 320, 640, 1280, 2560, 5120 s (λ_{ir} = 313 nm, l = 1 cm).

Table 2. Quantum Yields for the Photolysis of Butadiene Derivatives in Argon-Saturated *n*-Hexane (λ_{ir} = 313 nm)[a]

	compound[b]									
	c-**4**	*t*-**4**	*c,c*-**5**	*c,t*-**5**	*t,t*-**5**	*c,c*-**6**	*c,t*-**6**	*t,t*-**6**	*c*-**7**	*t*-**7**
Φ	0.75	0.31	0.14	0.11	0.29	0.13	0.16	0.13	0.013	0.040

[a] Standard deviation: ± 7%. [b] Abbreviations: *c* for *cis*, *t* for *trans*.

the quantum yield are in accordance with the fast isomerization of *cis,trans*-**5** to *cis,cis*-**5**, followed by the disappearance. For *trans,trans*-**5** the photochemical quantum yield is much higher (Φ = 0.29) than those for the other two isomers, indicating higher photoactivity of this derivative. Similar efficiency values, although a bit lower, were obtained for the 350 nm photolyses of these isomers (e.g., 0.11 for *trans,trans*-**5**). Connecting to this fact, the absorption spectra at the end of the photolyses (Figure 9) suggest that the composition of the final products from *trans,trans*-**5** are different from those of the other two isomers. These observations are in accordance with the results of product analysis indicating that the conformers of the *trans,trans*-isomer are favored for the formation of the final products (see later in Scheme 5).

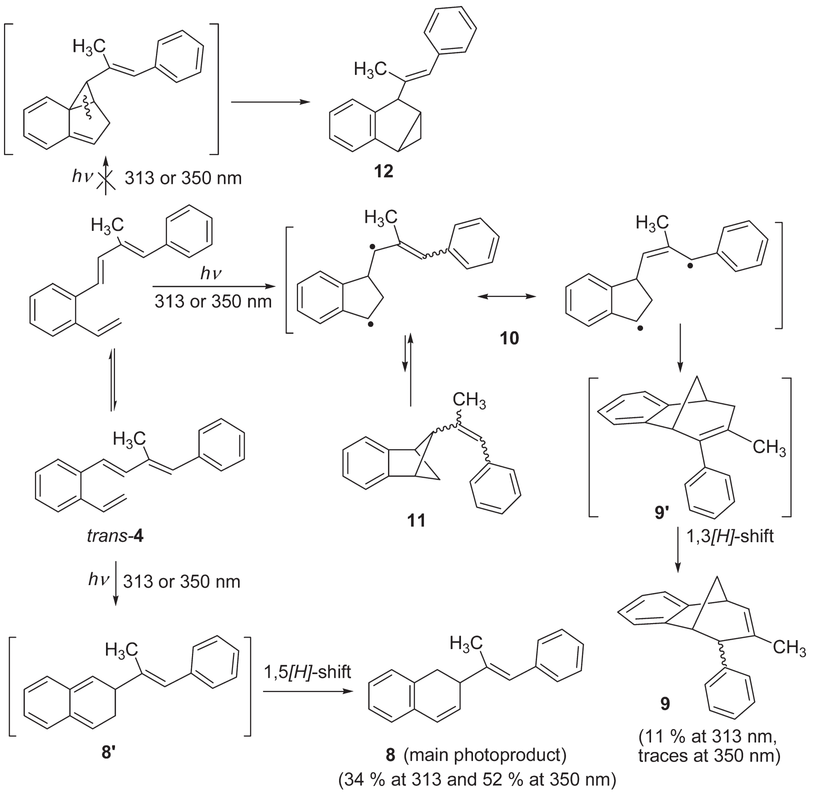
Upon excitation of *trans,trans*-**5** with a 5-ns laser pulse at 355 nm, a transient absorption of 450-ns lifetime was observed (Figure 10). On the basis of its relatively long lifetime and estimated absorption spectrum compared to those of the starting compound and the final product, this transient might be assigned to the triplet excited state of the initial compound. However, similarly to the case of *trans,trans*-**4**, the low efficiency of the ISC for DPB suggests the formation of another type of intermediate, probably a radical (see later in Scheme 5). The very short lifetime of the singlet excited state of *trans,trans*-**5** (τ_F = 0.2 ns) suggests that this reaction can take place during the laser pulse. The single-exponential decay of this intermediate indicates monomolecular reactions producing further intermediates or final products.

During the preparative photochemical experiment, introduction of the second styryl moiety results in the formation of bicyclo[3.2.1]octadiene structure **13**, the *trans,exo,endo*-isomer being predominant in 49% yield at 350 nm besides 10% of the corresponding *cis*-isomer (Scheme 5). Upon irradiation at 313 nm 20% of *trans*- and 30% of *cis,exo,endo*-**13** was detected according to NMR analyses followed by traces of *endo,endo*-**13** isomers. In the case of **5**, intramolecular cycloaddition reaction is the favorable photochemical path giving, besides *exo,endo*-**13**, the other stereoisomer *endo,endo*-**13** in traces. The formation of **13** is explained by the same mechanism (Scheme 5) as described for **9** (Scheme 4), from the preferred conformation of *trans,trans*-**5** via a 1,4-biradical **14** followed by the preferred cyclohexene ring closure to **15** and photochemically allowed suprafacial 1,3-H shift. The preferred ring closure with *endo*-orientation of the phenyl group can be ascribed to the stabilization of the transition state in an *endo*-orientation by the strong attractive intramolecular $\pi-\pi$ interactions of the benzo-phenyl groups, in both photoproducts.[47−49] The stereoselective formation of exactly the *exo,endo*-**13** with the *exo*-orientation of the unreacted styryl group can be explained (Scheme 5) by preferred *trans* ring closure to the indane intermediate **14**, presumably because of steric reasons, which then closes to yield *exo,endo*-**13** via **15**.

The formation of the *endo,endo*-isomer, found only in traces, was explained by *cis* ring closure to the indane intermediate **14′**, which via **15′** gave *endo,endo*-**13**. The proposed mechanism (Scheme 5) suggests the formation of the intermediate **14** from the *trans,trans*-**5**, which is in accordance with the photophysics showing that the all-*trans* configuration of **5** contributes the most to the relaxation via photochemical and internal conversion processes. Upon irradiation with higher energy more *cis,exo,endo*-**13** was formed confirming that the further trans−cis photoisomerization on the styryl group took place, after primary formation of *trans,exo,endo*-**13**.

After the complete conversion, the exact main photoproduct *trans,exo,endo*-**13** was separated and isolated by column chromatography on silica gel, and its structure was deduced unequivocally from spectral studies. From the ^{1}H and ^{13}C NMR spectra of *exo,endo*-**13**, using different techniques (COSY, NOESY, and HSQC), all protons and carbons were completely assigned. It can be seen the very well resolved four-proton pattern in the ^{1}H NMR spectrum between 3.2 and 4.1 ppm unmistakably points to the bicyclo[3.2.1]octadiene structure. The *exo*-orientation of the styryl at the methano bridge carbon is defined on the basis of COSY interaction between protons E and F (Figure 11). In previously obtained bicyclo[3.2.1]octadiene derivatives,[16,21] with no substituent on the methano bridge carbon, the proton E couples only with the *exo*-oriented proton F. As the *endo*-oriented proton does not couple with the proton E, the *exo*-structure was assigned. The *trans*-configuration on the styryl

Scheme 4. **Proposed Mechanism for the Photochemistry of *o*-Vinylbutadiene 4**



substituent on the methano bridge is confirmed by the existence of two coupling constants with 16.1 Hz for protons 1 and 2 (Figure 11). The signals in the lower field between 5.4 and 6.4 ppm are assigned to the A and B protons on double bond. One of the aromatic protons, H_{ar} of the benzo moiety is shifted to the higher field at 6.2 due to the anisotropic effect of phenyl *endo*-substituent. The *cis*-configuration on the styryl substituent of the other *exo,endo*-stereoisomer (Figure 11) is confirmed by the existence of two coupling constants with 11.9 Hz for protons 1 and 2. The small quantitiy of the diastereomer *endo,endo*-**13** is also well recognizable in ^{1}H NMR spectrum.

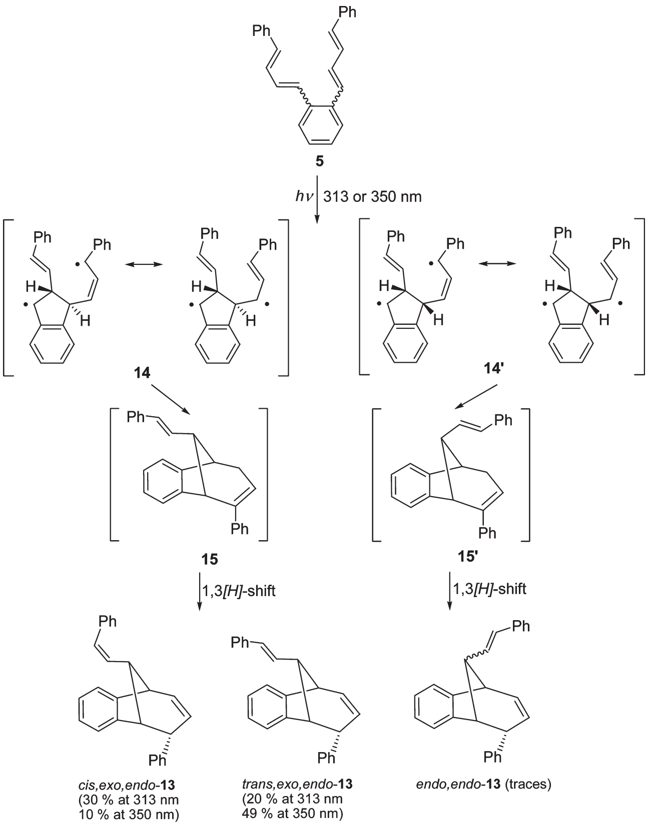
By introducing two methyl groups, both on the same double bond of the butadiene moiety to get the new starting material **6**, the influence of the substituent could be studied under the same conditions of intramolecular photochemical reaction as in the case of the starting compound **5**. In the initial period of irradiation, the behavior of the methyl-substituted derivatives **6** displays just the opposite tendency as that shown by the isomers of **5**. As seen in Figure 12, both *cis,cis*-**6** and *cis,trans*-**6** are efficiently transformed to *trans,trans*-**6**. This dramatic difference is caused by the methyl groups on the butadiene backbones, significantly reducing the extent of conjugation, leading to a nonplanar structure, also because of crowding. Thus, these molecular stuctures are less stable and more flexible than those of the derivatives **5**, making the photoinduced geometrical isomerization of both *cis,cis*-**6** and *cis,trans*-**6** possible. In this case the *trans,trans*-isomer is favored in the photostationary equilibrium. Accordingly, the quantum yields for the photochemical disappearance, from the quasi-photosationary state, are very similar at λ_{ir} = 313 nm (Table 2). The quantum yields at λ_{ir} = 350 nm are also similar to each other, with an average value of 0.10. Deviating from the case of derivatives **5**, the methyl groups in the isomers of **6** hamper the decay of the excited state via fluorescence (Φ_F <0.001), promoting vibrational energy dissipation due to the less rigid structure.

In flash photolysis experiments with *trans,trans*-**6**, several transient absorptions of significantly different lifetimes were observed. Similarly to the corresponding unsubstituted derivative (*trans,trans*-**5**), on the nanosecond time-scale a short-lived transient of 150-ns lifetime was recorded, which might be attributed to the formation and decay of triplet excited state (Figure 13). However, similarly to the cases of *trans,trans*-**4** and -**5**, this transient may be assigned to another type of intermediate, e.g., a radical species. The negligible fluorescence of *trans,trans*-**6** and the moderate quantum yields of its photochemical disappearance (Φ = 0.13 at λ_{ir} = 313 nm and 0.09 at λ_{ir} = 350 nm) suggest an appreciably efficient formation of this short-lived intermediate.

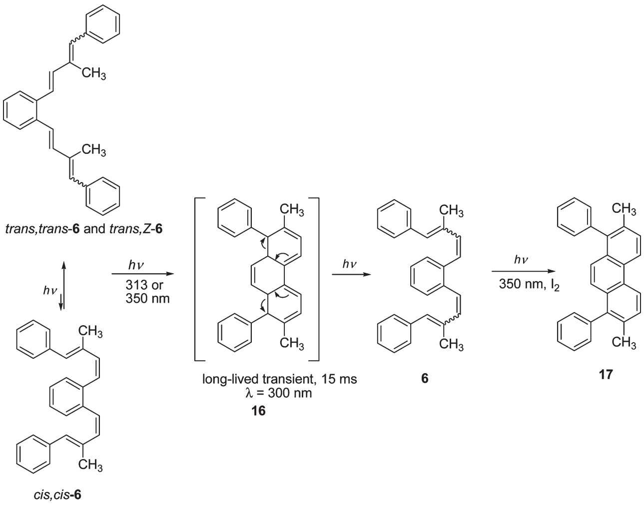
On a longer time scale, however, two other transients were observed with 50-μs and 15-ms lifetimes, respectively (Figure 14). On the basis of the lifetime and the change of the absorption, the decay of the latter intermediate probably leads to the formation of the final product in the photochemical reaction of the starting compound.

Contrary to the unsubstituted dibutadiene derivative **5**, introduction of the two methyl substituents resulted in different photoreaction of the starting molecule **6**, showing only photoisomerization upon irradiation (Scheme 6). On irradiation of the mixture of isomers of **6**, under the same conditions as for the starting material **5**, a different ratio of the geometric isomers of **6** was obtained. During the column chromatography in the first fractions *trans,Z*-**6** was isolated followed by *trans,trans*-**6** in the

Scheme 5. Proposed Mechanism for the Formation of the Bicyclo[3.2.1]octadiene Structures 13



Scheme 6. Mechanism Proposed for the Photochemistry of 6



last fractions, and the high-molecular-weight products remained on the column. Although only geometric isomerization was indicated by the product analysis, photoinduced disappearance of **6** from the quasi-photostationary state was observed in the 313 and the 313 nm photolyses with moderate quantum yields (average values of 0.14 and 0.10, respectively). This phenomenon may be attributed to photoinduced polymerization, which may easily occur between such dibutadiene units.

Regarding the mechanistic considerations,[50] the *cis,cis*-isomer of **6** being less preferred in the photostationary equilibrium during irradiation cyclizes to give intermediate **16**, which could be detected by laser flash photolysis and has a lifetime of several milliseconds (see Figure 14). Rearomatization of this intermediate to the starting compound **6** gives back the mixture of geometric isomers of **6**, in our case, *trans,Z*-**6** and *trans,trans*-**6**. This unique behavior of the methyl-substituted dibutadiene **6** could be ascribed to nonplanarity and different geometry of the starting material in comparison with **5**, also resulting in the absence of cycloaddition and/or electrocyclization reaction of **6**.

The steric influence of methyl groups is illustrated by comparison of the two most stable configurations (according to the observations at the beginning of the photolyses, Figures 9 and 12), *cis,cis*-**5** and *trans,trans*-**6**, whose structures were confirmed by X-ray structure analysis (Figure 15). Both compounds reveal molecular symmetry C_2 (in *cis,cis*-**5** the symmetry is approximate, whereas *trans,trans*-**6** possesses a crystallographic 2-fold rotation symmetry; details given in Supporting Information), and the conformations are twisted due to steric crowding of two α-methine groups bound to the central aromatic ring. While the *o*-dimethine moiety is nearly planar (α-methine carbons deviate less than 0.01 Å from the ring plane), the hydrogen atoms bound to them are twisted significantly out of plane. The distances between α-methine hydrogen atoms are 2.931 Å in *trans,trans*-**6**; in two symmetry-independent molecules of *cis,cis*-**5** they are 2.463 and 2.521 Å. Torsion angles between the two α-methinic C−H bonds are larger for *cis,cis*-**5** (86.0° and 84.5°, respectively) than for *trans,trans*-**6** (64.8°). Since methyl groups in *trans,trans*-**6** create very little steric strain, there is no reason to believe that geometry of *trans,trans*-**5** would differ significantly, especially in the central part of the molecule. However, the methyl groups in **6** complicate the situation. In a fictive model obtained by attaching methyl groups on the *cis,cis*-**5** methyl carbons would come as close as 2.6 Å to carbon atoms of the central aromatic ring, making the *cis,cis* configuration prohibitively strained. Therefore, *trans,trans* is energetically the most favorable configuration of **6**. An additional steric effect of the methyl groups can be noticed: the forcing of the terminal phenyl group out of the plane of the butadiene moiety. In *trans,trans*-**6** it is rotated relative to butadiene by 24.6° (Figure 15a), whereas in *cis,cis*-**5** the rotation is less than 5°.

If the experiment is performed at 350 nm from the starting compound **6** (as a mixture of isomers) but in the presence of iodine, 2,7-dimethyl-1,8-diphenylphenanthrene (**17**) was formed as a result of complete electrocyclization process from *cis,cis*-**6**. The structure of this symmetrical condensed aromatic system was obvious from the presence of the characteristic aromatic protons of phenanthrene moiety. As it is seen in the ^{1}H NMR spectrum, one doublet and one doublet of doublets appeared between 8.8 and 9.0 ppm with one signal for the methyl group in the lower magnetic field at 2.67 ppm. In the MS spectrum of **17**′, molecular ion *m/z* 360, 2 mass units lower than that of the starting compound **6**, indicated that an electrocyclization process and loss of a hydrogen molecule occurred.

Photolyses of derivatives **7** (Figure 16) display a similar tendency as was observed for compounds **4**. At the initial period of irradiation *cis*-**7** is transformed into *trans*-**7**, clearly indicated by the shift of the main band, whereas in the case of *trans*-**7** as starting material apparently no geometrical isomerization takes place. The main band gradually disappears during the irradiation as in all photolyses of the compounds in this study, indicating the

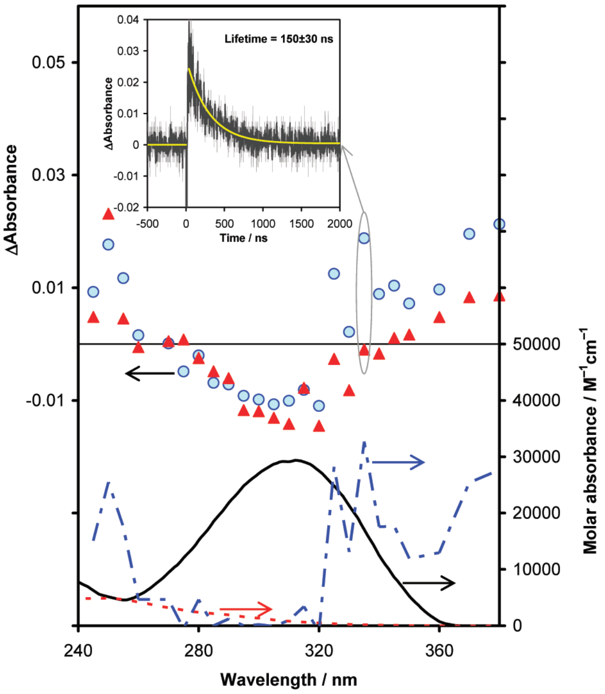


Figure 17. Transient absorption spectra of *trans*-**7** recorded at 100 ns (●) and 3000 ns (▲) after the excitation and the estimated spectrum of the short-lived intermediate (dash-dot line) along with the spectrum of the starting material (solid line) and that of the final product (dashed line). The decay curve at 335 nm (insert) is also displayed.

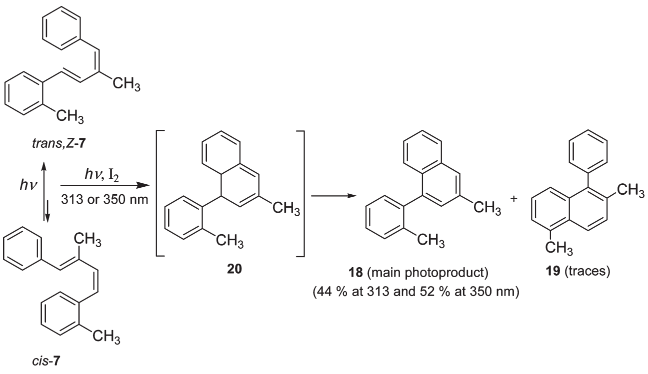
break of the long-range conjugation. The increase of absorbance at shorter wavelengths indicates the formation of new compounds containing less aromatic and conjugated parts. The quantum yields of the photoinduced disappearance of the starting derivatives **7** are rather low (0.013 for the *cis*- and 0.040 for the *trans*-isomer at λ_{ir} = 313 nm, 0.42, and 0.030 at λ_{ir} = 350 nm), similarly to the fluorescence efficiencies.

This phenomenon is in accordance with the nonplanar, more flexible structure with smaller extent of conjugation due to the effect of the methyl group on the butadiene moiety, promoting the nonradiative decay (energy dissipation) of the excited state.

Similarly to the other derivatives in this study, flash photolysis experiments with *trans*-**4** resulted in significant transient absorption changes in the nanosecond time scale (Figure 17a). Also in this case, on the basis of its lifetime (280 ± 30 ns, Figure 17b) and estimated absorption spectrum compared to those of the starting compound and the final product (Figure 17a), this transient might be assigned to the triplet excited state of the initial compound. Similarly to the previous cases, however, on the basis of the inefficient ISC, this transient may be attributed to a chemically formed species, e.g., a radical or an isomer intermediate (see in Scheme 7). The rather short lifetime of the singlet excited state of *trans*-**7** (τ_{F} = 1.09 ns) indicates that the formation of this species can take place within the 5-ns duration of the laser pulse. The low fluorescence quantum yield (0.02) of this isomer suggests an efficient formation of this intermediate.

The preparative photochemical reaction of the model compound **7**, methyl analogue of 2-methyl-1-(*o*-vinylphenyl)-4-phenylbutadiene derivative **4**, gave substituted arylnaphthalenes **18** and **19** as is expected under aerobic conditions (Scheme 7).[12,13] Irradiation of 3×10^{-3} M solution of **7** (as mixture of isomers) in dry toluene containing iodine gave, after 15 h, the mixture of phenylnaphthalenes **18** and **19**, with the former being predominant. As shown in the Scheme 6, photocyclization can occur to the substituted phenyl ring from *trans,Z*-**7** to give **18** and to the unsubstituted phenyl ring from *cis*-**7** to give **19**. The photoreaction of **7** gave the phenylnaphthalene **18** in 52% of isolated yield besides traces of **19**, along with the formation of some dimeric and polymeric products, which were not further investigated. The formation of both phenylnaphthalene **18** and **19** can be explained by electrocyclization process from different conformations of *cis* configuration (Scheme 7) followed by an aromatization step with concomitant loss of hydrogen.[51,52]

Scheme 7. Photochemical Reactions of Compound 7



The photoproduct **18** was isolated by column chromatography and characterized spectroscopically. The structure was obvious from the presence of two characteristic singlets of aromatic protons of the naphthalene moiety in the ^{1}H NMR spectrum characteristic only for **18**. In the ^{1}H NMR spectrum of some enriched chromatographic fractions traces of the recognizable naphthalene pattern of **19** have been seen but in too small quantities to be better identified. Additionally, MS spectra were very informative. Molecular ions *m*/*z* 244 for both cyclization products, 2 mass units lower than for starting compounds **7**, indicated that an electrocyclization process and loss of hydrogen molecule happened. These data clearly revealed that photocyclization occur to the substituted phenyl ring from *trans,Z*-**7**.

It should be noted that in the absence of I_2 only geometric isomerization takes place upon irradiation of **7**. This observation is in accordance with the very low quantum yields (in the order of hundredths) for the photoinduced disappearance of these isomers (from the quasi-photostationary equilibrium), which may be attributed to polymerization, similarly to the case of **6**. However, the chance for polymerization of **7** is much lower because of the presence of one instead of two butadiene units. This is manifested in the 1 order of magnitude lower quantum yields.

■ CONCLUSIONS

The versatile photoinduced behavior of butadiene derivatives has been revealed by the diverse photochemistry and photophysics of four compounds of rather similar structures. The results reveal that the introduction of a substituent in the parent compound **1** changes the course of the photoreaction in several instances. The introduction of the second styryl substituent at the β-position of the vinyl group of **1** does not influence the cycloaddition reaction qualitatively; however, the compound **5** gives the main benzobicyclo photoproduct in a strongly lowered yield in comparison with **1**. Introduction of a methyl group at the second double bond of **1** leads to the formation of electrocyclization product **8**, whereas two methyl groups introduced to **5**, causing nonplanarity and steric crowding, totally hinders the photocycloaddition in **6**, resulting in geometric isomerization as the only photochemical reaction. These dramatic effects of the methyl group on the photochemical features are in accordance with those on the photophysical properties due to the reduction of the conjugation and planarity of the molecule. Since methyl substituent(s) had no direct electronic influence on the reaction, the differences between the reactions of the individual compounds had to be ascribed to steric factors. Furthermore, it can be considered that variations in the ground-state conformations of the compounds investigated are responsible for their diverse photobehavior. In the case of the studied butadiene systems, the excitation of conformers of each derivative at the two excitation wavelengths is probably selective but without considerable photochemical and photophysical consequences. Understanding of the governing effects of the substituents on the photochemical reactions of these new butadiene derivatives and elucidation of their reaction mechanisms make the synthesis of these systems suitable for directing the photoreaction to different interesting structures that can be further transformed and functionalized.

EXPERIMENTAL SECTION

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions containing tetramethylsilane as internal standard at 300 or 600 and at 75 or 150 MHz, respectively. The mass spectra were recorded on a GC−MS instrument (GC temperature program: delay 3 min, injector temperature 350 °C, heating from 110 to 300 °C within 6 min, then 300 °C isothermal for 7 min). High-resolution mass spectra (HRMS) were obtained on a matrix-assisted laser desorption/ionization time-of-flight MALDI-TOF/TOF mass spectrometer equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive ion reflector mode; 1600 shots per spectrum were taken with mass range 100−1000 Da, focus mass 500 Da and delay time 100 ns. Nicotinamide and azithromycin were used for external mass calibration in positive ion mode. Each spectrum was internally calibrated, providing measured mass accuracy within 5 ppm of theoretical mass. Melting points are uncorrected. All preparative irradiation experiments were carried out with about 10^{-3} molar solutions in a quartz tube and in a photochemical reactor equipped with UV lamps. For quantum yield measurements a photolysis equipment, containing a 200 W XeHg lamp and a monochromator was used.[53] Irradiation wavelengths were 313 and 350 nm. Incident light intensity was determined with a thermopile calibrated by ferrioxalate actinometry.[54,55] Typically, the irradiations were carried out with 3.5-cm^3 solutions of about 10^{-4} M concentration in 1-cm cells at room temperature. HPLC grade *n*-hexane were used as solvents in these experiments. During the photolyses the reaction mixtures were continuously homogenized by magnetic stirring. Following the change of the absorption spectrum of the solution photolyzed, the quantum yield for the photochemical transformation of the starting material was determined from the initial rate calculated from the absorbance versus time plot at a characteristic wavelength where the products did not absorb.

Absorption spectra were recorded by using a double-beam and a diode array spectrophotometer. For the measurement of fluorescence spectra a high-sensitivity spectrofluorimeter was applied. This equipment supplemented with a time-correlated single-photon counting accessory was applied for determination of fluorescence lifetimes too. $Ru(bpy)_3Cl_2$,[56] quinine bisulphate (in 0.5 M H_2SO_4), and 9,10-diphenylanthracene[57] were utilized as references for determination of the fluorescence quantum yields. Each compound studied was excited at the wavelength of its absorption maximum. Luminescence spectra were corrected for detector sensitivity.

Transient absorption measurements were carried out with a laser flash photolysis system, which involved a Nd:YAG laser yielding 355 nm pulses of about 5 ns duration and a digital oscilloscope system. The molar absorption spectra of the short-lived intermediates detected by flash photolysis was estimated by compensation of the bleaching. Since the absorption spectra of the intermediates significantly overlap with those of the corresponding ground-state starting compounds and thus the concentration of the intermediate formed could not be reliably determined, a very rough estimation was made for it. In the case of each compound studied by flash photolysis, at the wavelength at which the transient absorbance decrease after the light pulse divided by the molar absorbance of the starting compound gave the highest value, the molar absorbance of the short-lived intermediate was taken to be zero. Hence, the absorbance decrease at this wavelength was exclusively estimated by the bleaching of the starting compound. Although the molar absorbances estimated in this way for the intermediate are the minimum possible values, the positions of the bands have been reliably determined. Chromatographic separations were perfomed on silica gel columns (0.063−0.2 mm) and thin layer plates (silica gel 0.2 mm). All solvents were distilled prior the use. The starting compounds *trans*-cinnamaldehyde, *trans*-α-methyl-cinnamaldehyde, and paraformaldehyde were purchased from a commercial source, and known procedures were used to prepare *o*-methylbenzyltriphenylphosphonium bromide from the corresponding bromide and diphosphonium salt of α,α'-*o*-xylylenedibromide.

1-(3-Methyl-4-phenylbuta-1,3-dienyl)-2-vinylbenzene (4). To a stirred solution of α,α'-*o*-xylyl(ditriphenylphosphonium) bromide (7.380 g, 9.36 mmol) and *trans*-α-methyl-cinnamaldehyde (1.53 g, 10.30 mmol) in absolute ethanol (100 mL) was added a solution of sodium etoxide (0.23 g, 10.0 mmol in 20 mL ethanol) dropwise. Stirring was continued under a stream of nitrogen for 1 h at rt. Under the stream of nitrogen gaseous formaldehyde (obtained by the decompostion of an excess of paraformaldehyde, 1.41 g, 46.7 mmol) was introduced, and an additional quantity of sodium etoxide (0.23 g, 10.0 mmol in 20 mL ethanol) was added. After removal of the solvent, the residue was worked up with water and benzene. The benzene extract was dried and concentrated. The crude reaction mixture was purified, and the mixture of isomers was isolated in 65% yield (24% *cis*- and 76% *trans*-isomer according to ^{1}H NMR). The mixture of isomers was separated by column chromatography on silica gel using petroleum ether as eluent.

cis-**4**: colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 279 (13456); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.52 (d, 1H, J = 7.7 Hz, H_{ar}), 7.33−7.27 (m, 3H, H_{ar}), 7.21−7.16 (m, 3H, H_{ar}), 7.13−7.11 (m, 1H, H_{ar}), 7.03−7.00 (m, 1H, H_{ar}), 6.95 (dd, 1H, J_{13} = 17.6 Hz, J_{23} = 10.9 Hz, H_3), 6.54 (d, 1H, J = 12.1 Hz, H-A/B), 6.52 (broad s, 1H, H−C), 6.42 (d, 1H, J = 12.1 Hz, H-A/B), 5.70 (dd, 1H, J_{13} = 17.6 Hz, J_{12} = 1.1 Hz, H_2), 1.68 (d, 3H, J = 1.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 136.4 (d), 135.3 (d), 132.7 (d), 129.1 (2d), 128.1 (d), 128.0 (2d), 127.9 (d), 127.6 (d), 127.1 (d), 126.5 (d), 125.0 (d), 115.0 (t), 17.8 (q), singlets are not seen due to small quantities; MS *m*/*z* (EI) 246 (M^+, 100%), 231 (20), 117 (30).

trans-**4**: colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 315 (29537); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.52 (d, 1H, J = 7.6 Hz, H_{ar}), 7.46 (d, 1H, J = 7.6 Hz, H_{ar}), 7.38−7.32 (m, 5H, H_{ar}), 7.28−7.24 (m, 2H, H_{ar}), 7.07 (dd, 2H, J_{13} = 17.5 Hz, J_{23} =11.1 Hz, H_3), 6.94 (d, 1H, J = 16.2 Hz, H-A/B), 6.85 (d, 1H, J = 16.2 Hz, H-A/B), 6.66 (broad s, 1H, H−C), 5.64 (dd, J_{13} = 17.5 Hz, J_{12} = 1.3 Hz, H_1), 5.35 (dd, J_{23} = 11.1 Hz, J_{12} = 1.3 Hz, H_2), 2.14 (d, 3H, J = 1.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.3 (s), 136.0 (d), 135.8 (s), 135.6 (s), 135.4 (s), 134.6 (d), 131.9 (d), 128.8 (2d), 127.7 (2d), 127.3 (d), 126.9 (d), 126.2 (d), 126.1 (d), 125.6 (d), 125.1 (d), 115.8 (t), 13.5 (q); MS *m*/*z* (EI) 246 (M^+, 100%), 231 (25), 117 (20); HRMS (TOF ES^+) *m*/*z* calculated (for the mixture of geometrical isomers of **4**) for $C_{19}H_{18}$ 246.0910, found 246.0914.

1,2-Bis(4-phenylbuta-1,3-dienyl)benzene (5) and 1,2-Bis-(3-methyl-4-phenylbuta-1,3-dienyl)benzene (6). To a stirred solution of α,α'-*o*-xylyl(ditriphenylphosphonium) bromide (4.472 g, 5.50 mmol) and corresponding aldehydes (*trans*-cinnamaldehyde and *trans*-α-methyl-cinnamaldehyde, 1.5 g, 11.0 mmol) in absolute ethanol (100 mL) was added a solution of sodium etoxide (0.261 g, 11.35 mmol in 20 mL ethanol) dropwise. Stirring was continued overnight at rt. After removal of the solvent on a rotary evaporator, the residue was worked up with water (20 mL) and benzene (3 × 30 mL). The benzene extract were dried over $MgSO_4$ and concentrated. The crude reaction mixture was purified, and products were isolated in 91% yield (7% *cis,cis*-, 45% *cis,trans*-, and 48% *trans,trans*-isomer according to ^{1}H NMR) for **5** (1.488 g) and 81% yield (10% *cis,cis*, 50% *cis,trans*, and 40% *trans,trans* according to ^{1}H NMR) for **6** (1.812 g). The mixture of isomers was separated by TLC or repeated column chromatography on silica gel using petroleum ether as eluent.

cis,cis-**5**: white crystals; mp 65−67 °C; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 285 (6816); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.35 (d, 4H, J = 7.7 Hz, H$_{ar}$), 7.28 (t, 4H, J = 7.7 Hz, H$_{ar}$), 7.23−7.19 (m, 6H, H$_{ar}$), 7.09 (dd, 2H, J = 15.6 Hz, J = 10.8 Hz, H$_C$), 6.69 (d, 2H, J = 15.6 Hz, H$_D$), 6.57 (d, 2H, J = 11.2 Hz, H$_A$), 6.47 (dd, 2H, J = 11.2, J = 10.7 Hz, H$_B$); ^{13}C NMR (CDCl$_3$, 75 MHz, ppm) δ 137.8 (s), 136.6 (s), 134.2 (d), 130.4 (d), 130.0 (d), 129.8 (d), 129.7 (d), 128.6 (2d), 127.6 (d), 127.3 (d), 126.5 (d), 125.5 (d); MS m/z (EI) 334 (M$^+$, 100%), 206 (15).

cis,trans-**5**: white crystals; mp 72−74 °C; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 318 (30120); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.55 (d, 2H, J = 7.6 Hz, H$_{ar}$), 7.44 (d, 4H, J = 7.6 Hz, H$_{ar}$), 7.33 (t, 4H, J = 7.6 Hz, H$_{ar}$), 7.23 (t, 2H, J = 7.6 Hz, H$_{ar}$), 7.21−7.14 (m, 2H, H$_{ar}$), 7.99 (dd, 2H, J = 15.8 Hz, J = 9.0 Hz, H$_B$, H$_C$), 6.89 (d, 1H, J = 16.0 Hz, H$_{A/D/D'}$), 6.88 (d, 1H, J = 12.0 Hz, H$_{A'}$), 6.87−6.84 (m, 2H, H$_{B'}$, H$_{C'}$), 6.68 (d, 2H, J = 15.8 Hz, H$_{A/D/D'}$); ^{13}C NMR (CDCl$_3$, 75 MHz, ppm) δ 133.4 (d), 132.9 (d), 132.6 (d), 131.4 (d), 130.9 (d), 130.1 (d), 129.7 (d), 129.4 (d), 129.1 (d), 128.7 (d), 128.5 (2d), 128.0 (d), 127.8 (d), 127.4 (d), 127.1 (d), 126.7 (2d), 126.6 (d), 125.9 (d) (singlets are not seen due to small quantities); MS m/z (EI) 334 (M$^+$, 100%), 206 (10).

trans,trans-**5**: yellow-green crystals; mp 169−170 °C; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 303 (23369); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.59−7.49 (m, 4H, H$_{ar}$), 7.49−7.42 (m, 4H, H$_{ar}$), 7.34 (t, 4H, J = 7.4 Hz, H$_{ar}$), 7.25−7.21 (m, 2H, H$_{ar}$), 7.03 (dd, 2H, J = 15.6 Hz, J = 10.3 Hz, H$_C$), 7.02 (d, 2H, J = 15.1 Hz, H$_A$), 6.85 (dd, 2H, J = 15.1 Hz, J = 10.3 Hz, H$_B$), 6.70 (d, 2H, J = 15.6 Hz, H$_D$); ^{13}C NMR (CDCl$_3$, 75 MHz, ppm) δ 137.3 (s), 135.6 (s), 133.1 (d), 131.6 (d), 130.3 (d), 129.5 (d), 128.7 (2d), 128.6 (d), 127.6 (d), 126.4 (2d), 126.3 (d); MS m/z (EI) 334 (M$^+$, 100%); HRMS (TOF ES$^+$) m/z calculated (for the mixture of geometrical isomers of **5**) for $C_{26}H_{22}$ 334.1207; found 334.1199.

cis,cis-**6**: yellow oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 299 (30752); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.32−7.28 (m, 4H, H$_{ar}$), 7.24−7.21 (m, 6H, H$_{ar}$), 7.19−7.14 (m, 4H, H$_{ar}$), 6.53 (broad s, 2H, H−C), 6.50 (d, 2H, J = 12,1 Hz, H-A/B), 6.37 (d, 2H, J = 12.1 Hz, H-A/B), 1.79 (d, 6H, J = 1.2 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) δ 137.3 (s), 136.7 (s), 135.1 (d), 135.0 (s), 131.7 (d), 129.0 (d), 128.6 (2d), 127.7 (d), 127.6 (2d), 126.1 (d), 126.0 (d), 17.7 (q); MS m/z (EI) 362 (M$^+$, 100%).

cis,trans-**6**: yellow oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 291 (12229); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.60 (d, 1H, H$_{ar}$), 7.36−7.32 (m, 2H, H$_{ar}$), 7.31−7.28 (m, 3H, H$_{ar}$), 7.25−7.21 (m, 6H, H$_{ar}$), 7.20−7.16 (m, 2H, H$_{ar}$), 6.94 (d, 1H, J = 15.9 Hz, H-A′/B′), 6.90 (d, 1H, J = 15.9 Hz, H-A′/B′), 6.66 (broad s, 1H, H−C′), 6.58 (d, 1H, J = 12.2 Hz, H-A/B), 6.56 (broad s, 1H, H−C), 6.47 (d, 1H, J = 12.2 Hz, H-A/B), 2.09 (d, 3H, J = 1.0 Hz, CH$_3$′), 1.70 (d, 3H, J = 1.1 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) δ 137.4 (s), 137,2 (s), 136,9 (s), 136,1 (d), 135,8 (s), 135,4 (s), 135,3 (s), 134,8 (d), 132,3 (d), 131,8 (d), 129,5 (2d), 128,7 (2d), 128,6 (2d), 127,6 (d), 127,5 (2d), 127,4 (d), 126,8 (d), 126,2 (d), 126,1 (d), 126,0 (d), 125,9 (d), 124,4 (d), 17,4 (q), 13.4 (q); MS m/z (EI) 362 (M$^+$, 100%).

trans,trans-**6**: white crystals; mp 93−95 °C; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 298 (27188); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.52 (m, 2H, H$_{ar}$), 7.38−7.32 (m, 8H, H$_{ar}$), 7.24−7.22 (m, 4H, H$_{ar}$), 6.99 (d, 2H, J = 15.9 Hz, H-A/B), 6.87 (d, 2H, J = 15.9 Hz, H-A/B), 6.67 (široki s, 1H, H−C), 2.16 (d, 6H, J = 0.9 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) δ 137.4 (s), 136.1 (d), 135.7 (s), 135.6 (s), 132.0 (d), 128.8 (2d), 127.7 (2d), 126.9 (d), 126.2 (d), 126.0 (d), 125.4 (d), 13.6 (q); MS m/z (EI) 362 (M$^+$, 100%); HRMS (TOF ES$^+$) m/z calculated (for the mixture of geometrical isomers of **6**) for $C_{28}H_{26}$ 362.1414, found 362.1401.

1-Methyl-2-(3-methyl-4-phenylbuta-1,3-dienyl)benzene (7). To a stirred solution of *o*-tolyl-(benzyltriphenylphosphonium)bromide (7.38 g, 9.26 mmol) and *trans*-α-methyl-cinnamaldehyde (1.53 g, 10.30 mmol) in absolute ethanol (100 mL) was added a solution of sodium ethoxide (0.23 g, 10.0 mmol in 20 mL ethanol) dropwise, and the mixture was stirred for 3 h at rt. After removal of solvent an extraction with benzene was carried out. The extract was dried and concentrated. The crude reaction mixture was purified, and the mixture of *cis*- and *trans*-isomers of the compound **7** was separated by column chromatography on silica gel using petroleum ether as eluent. The product **7** was isolated in 77% yield (27% *cis*- and 73% *trans*-isomer according to ^{1}H NMR).

cis-**7**: colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 289 (21775); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.30 (t, 2H, J = 7.6 Hz, H$_{ar}$), 7.24−7.10 (m, 7H, H$_{ar}$), 6.52 (broad s, 1H, H−C), 6.49 (d, 1H, J = 12.2 Hz, H-A/B), 6.38 (d, 1H, J = 12.2 Hz, H-A/B), 2.30 (s, 3H, CH$_3$′), 1.69 (d, 3H, J = 1.2 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) δ 136.6 (s), 135.0 (d), 132.9 (s), 131.8 (d), 131.7 (s), 129.0 (d), 128.9 (d), 128.6 (2d), 128.0 (d), 127.9 (s), 127.5 (d), 126.5 (d), 125.9 (2d), 124.7 (d), 19.5 (q), 17.3 (q); MS m/z (EI) 234 (M+, 100%), 219 (25), 143 (15), 115 (15).

trans-**7**: white crystals; mp 63−64 °C; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 312 (29350); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.56 (d, 1H, J = 7.1 Hz, H$_{ar}$), 7.40−7.31 (m, 4H, H$_{ar}$), 7.24−7.12 (m, 4H, H$_{ar}$), 6.88 (ABq, 2H, J = 16.2 Hz, H-A, H−B), 6.67 (broad s, 1H, H−C), 2.40 (s, 3H, CH$_3$′), 2.15 (d, 3H, J = 1.1 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 75 MHz, ppm) δ 137.9 (s), 136.6 (s), 136.1 (s), 135.6 (s), 135.5 (d), 132.2 (d), 130.4 (d), 129.3 (2d), 128.2 (2d), 127.2 (d), 126.6 (d), 126.2 (d), 125.6 (d), 125.2 (d), 19.9 (q), 14.0 (q); MS m/z (EI) 234 (M+, 100%), 219 (25), 143 (10), 115 (10); HRMS (TOF ES$^+$) m/z calculated (for the mixture of geometrical isomers of **7**) for $C_{18}H_{18}$ 234.1050;, found 234.1045.

Photochemistry of Compound 4. A mixture of isomers of **4** in petroleum ether (6.0×10^{-3} M) was purged with argon for 20 min and irradiated in Rayonet reactor at 313 or 350 nm in a quartz tube for 20 h. Solvent was removed in vacuum, and the residue was chromatographed on silica gel column using petroleum ether as eluent. After repeated column chromatography photoproduct **8** was isolated in the first fractions in 34% at 313 nm and 52% at 350 nm yield, while the minor photoproduct **9** was obtained in the last fractions in 11% yield at 313 nm and in traces at 350 nm according to NMR analyses.

(*E*)-2-(1-phenylprop-1-en-2-yl)-1,2-dihydronaphthalene (8). Colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 256 (5311); ^{1}H NMR (CDCl$_3$, 600 MHz, ppm) δ 7.40−7.08 (m, 10H), 6.77 (d.d., 1H, J = 5.4; 1.7 Hz, H$_F$), 6.39 (dd, 1H, J = 5.4; 2.0 Hz, H$_E$), 4.88 (dd, 1H, J = 9.8; 1.3 Hz, H$_D$), 4.46 (dt, 1H, J = 9.8; 2.0 Hz, H$_C$), 3.73 (d, 1H, J = 14.6 H$_A$/H$_B$), 3.63 (d, 1H, J = 14.6 H$_A$/H$_B$), 1.70 (d, 1H, J = 1.3 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) δ 144.3 (s), 144.1 (s), 139.9 (s), 138.8 (d), 137.1 (s), 131.4 (d), 128.9 (2d), 128.5 (d), 126.7 (2d), 126.1 (d), 125.0 (d), 123.7 (d), 123.3 (d), 121.0 (d), 50.1 (d), 38.4 (t), 23.6 (q); MS m/z (EI) 246 (M$^+$, 100%), 102 (45); HRMS (TOF ES$^+$) m/z calculated for $C_{19}H_{18}$ 246.0894, found 246.0899.

Photochemistry of Compound 5. A mixture of isomers of **5** in petroleum ether (2×10^{-3} M) was purged with argon for 20 min and irradiated at 313 or 350 nm in a Rayonet reactor in a quartz tube for 15 h. After irradiation the solvent was removed in vacuo, and the oily residue was chromatographed on silica gel using petroleum ether/diethyl ether (3%). The major isolated product at 350 nm was bicyclic derivative *trans,exo,endo*-**13** in 49% yield in addition to 10% of the corresponding *cis*-isomer. Upon irradiation at 313 nm, in the first fractions 20% of *trans*- and 30% of *cis,exo,endo*-**13** was isolated according to NMR analyses, followed with traces of *endo,endo*-**13** isomers. High-molecular-weight products remained on the column.

6-*endo*-Phenyl-10-*exo*-styryl-6,9-dihydro-5*H*-5,9-methano-benzocycloheptene (*trans,exo,endo*-13). Colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 254 (15655); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.24−7.11 (m, 7H H_{ar}), 7.06 (dt, 2H, J = 7.4 Hz, J = 1.0 Hz, H_{ar}), 6.83 (dt, 1H, J = 7.4 Hz, J = 1.0 Hz, H_{ar}), 6.76−6.72 (m, 3H, H_{ar}), 6.50 (d, 1H, J = 16.1 Hz, H_1), 6.44 (ddd, 1H, J = 9.5 Hz, J = 6.7 Hz, 2.5 Hz, H_A), 6.18 (d, 1H, J = 7.3 Hz, $H_{ar'}$), 6.02 (dd, 1H, J = 16.1 Hz, J = 8.7 Hz, H_2), 5.38 (dt, 1H, J = 9.5 Hz, J = 2.5 Hz, H_B), 4.07 (ddd, 1H, J = 4.6 Hz, J = 2.5 Hz, J = 2.5 Hz, H_C), 3.79 (d, 1H, J = 9.7 Hz, H_E), 3.30 (d,1H, J = 4.6 Hz, H_D), 3.23−3.21 (m, 1H, H_F); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 150.1 (s), 141.3 (s), 139.5 (s), 139.0 (s), 134.4 (d), 131.9 (d), 129.9 (d), 128.0 (2d), 127.9 (d), 127.3 (2d), 126.6 (d), 126.5 (d), 126.2 (d), 126.0 (d), 125.8 (2d), 125.6 (2d), 124.9 (d), 120.6 (d), 58.5 (d), 54.0 (d), 46.8 (d), 46.1 (d); MS m/z (EI) 334 (M$^+$, 100%), 206 (45); HRMS (TOF ES$^+$) m/z calculated for $C_{26}H_{22}$ 334.1406, found 334.1412.

Photochemistry of Compound 6. In a quartz tube, the mixture of isomers of **6** was dissolved in petroleum ether (3.4×10^{-3} M), purged with argon for 20 min, and irradiated at 313 or 350 nm for 15 or 22 h, respectively. The residue after evaporation of the solvent was chromatographed on a column filled with silica gel using petroleum ether/diethyl ether (0−2%) as eluent. After irradiation at 350 nm, in the first fraction the new geometric isomer *trans,Z*-**6** was isolated (0.032 g, 41%), followed by the starting *trans,trans*-isomer of **6** (0.039 g, 50%). At 313 nm the yields of *trans,Z*-**6** and *trans,trans*-**6** were 32% and 45%, respectively. In both cases, high-molecular-weight products remained on the column.

1,2-Bis((1*E*,3*Z*)-3-methyl-4-phenylbuta-1,3-dienyl)benzene (*trans,Z*-6). Yellow oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 294 (8989); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.39−7.34 (m, 1H), 7.33 (d, 2H, J = 7.2 Hz), 7.30 (d, 2H, J = 7.2 Hz), 7.22 (t, 1H, J = 7.2 Hz), 7.20 (d, 1H, J = 16.6 Hz), 7.16 (m, 1H), 7.01 (d, 1H, J = 16.6 Hz), 6.57 (s, 1H), 2.14 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.1 (s), 135.8 (s), 134.3 (s), 130.2 (d), 129.2 (d), 128.9 (2d), 127.7 (d), 127.6 (2d), 126.9 (d), 126.2 (d), 126.1 (d), 20.6 (q); MS m/z (EI) 362 (M$^+$, 100%); HRMS (TOF ES$^+$) m/z calculated for $C_{28}H_{26}$ 362.0907, found 362.0913.

Photochemistry of Compound 7. A mixture of isomers of **7** was dissolved in toluene (6.4×10^{-3} M). The solution was purged with argon for 20 min, or without argon and with catalytic amount of I_2, and irradiated at 313 or 350 nm in a Rayonet reactor in a quartz tube for 15 h. The irradiation of derivative **7** in the presence of iodine resulted in a formation of two photoproducts **18** (52% (0.08 g) isolated yield was found at 350 nm and 44% at 313 nm) and **19** only in traces. Solvent was removed in vacuo, and the photoproduct **18** was isolated in the last fractions by repeated chromatography combined on a silica gel column and thin layer silica gel using petroleum ether as eluent. Unreacted starting compound **7** was isolated in the first fractions. High-molecular-weight products remained on the column. The irradiation of derivative **7** in the deaerated solution resulted only in photoisomerization to a mixture of *trans*-**7** and 1-methyl-2-((1*E*,3*Z*)-3-methyl-4-phenylbuta-1,3-dienyl)benzene (*trans,Z*-**7**).

3-Methyl-1-*o*-tolylnaphthalene (18). Colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 250 (4911); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.80 (d, 1H, J = 8.3 Hz), 7.62 (s, 1H), 7.42 (dt, 1H, J = 7.4; 1.2 Hz), 7.39 (d, 1H, J = 7.4 Hz), 7.30−7.26 (m, 4H), 7.20 (t, 1H, J = 7.4 Hz), 7.17 (d, 1H, J = 1.5 Hz), 2.54 (s, 3H, CH_3), 2.02 (s, 3H, CH_3); MS m/z (EI) 232 (M$^+$, 100%); HRMS (TOF ES$^+$) m/z calculated for $C_{18}H_{16}$ 232.1007, found 232.1012.

1-Methyl-2-((1*E*,3*Z*)-3-methyl-4-phenylbuta-1,3-dienyl)-benzene (*trans,Z*-7). Colorless oil; UV (*n*-hexane) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 293 (23237); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.55 (d, 1H, J = 7.1 Hz), 7.36−7.31 (m, 4H), 7.20−7.13 (m, 4H), 6.87 (AB_q, 2H, J = 15.3 Hz), 6.66 (s, 1H), 2.40 (s, 3H, CH_3), 2.15 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.4 (s), 136.2 (s), 135.6 (s), 135.1 (s), 134.9 (d), 131.7 (d), 129.9 (d), 128.8 (2d), 127.7 (2d), 126.7 (d), 126.1 (d), 125.7 (d), 125.2 (d), 124.7 (d), 20.7 (q), 19.4 (q); MS m/z (EI) MS m/z (EI) 234 (M$^+$, 100%), 219 (35), 143 (10), 115 (15); HRMS (TOF ES$^+$) m/z calculated for $C_{18}H_{18}$ 234.0040, found 234.0049.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** ^{1}H NMR and ^{13}C NMR spectra for compounds **4**−**8**, **13**, and **18** and crystallographic data for *cis,cis*-**5** and *trans,trans*-**6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

†Dedicated to Professor Marija Šindler-Kulyk on the occasion of her 70th birthday.

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