

The Photochemical *cis-trans* Isomerization of Substituted Dibenzylidenesuccinic Anhydrides

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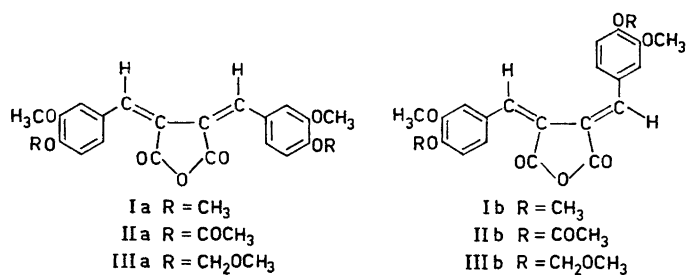
The photochemical isomerization of α,α' -diveratrylidenesuccinic anhydride (diveratryl fulgide), α,α' -di(acetylguajacylidene)-succinic anhydride and α,α' -di(methoxymethylguajacylidene)succinic anhydride is described. Structural assignments for the *trans-trans* and *cis-trans* isomers are made with the aid of NMR spectra. The chemical shifts of the vinyl proton signals are correlated with charge densities calculated by the Hückel molecular orbital method. Some regularities occurring in the infrared and ultraviolet spectra are described.

The diarylidenesuccinic anhydrides belong to a class of compounds called "fulgides" by Stobbe¹ who first synthesized a number of these compounds. The corresponding dicarboxylic acids, the "fulgic acids", are synthesized by condensation of diethyl succinate with aromatic aldehydes in the presence of sodium metal, sodium alkoxides, or potassium *t*-butoxide.² This reaction, the Stobbe condensation, has been reviewed by Johnson and Daub.³ The fulgic acids are converted to fulgides by boiling with acetyl chloride or acetic anhydride.

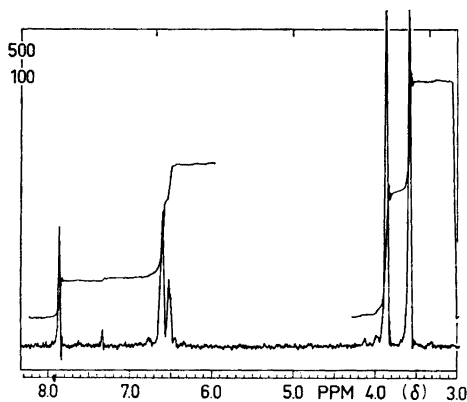
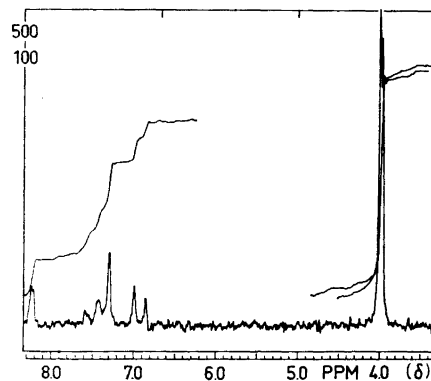
The aromatic fulgides are strongly coloured, yellow, orange or red when solid, and give intensely yellow solutions. When the fulgides are irradiated with sunlight or ultraviolet light, they are converted to more strongly coloured products. This reaction was ascribed to *cis-trans* isomerization already by Stobbe,⁴ but no structural assignments were made at that time. More recently, structural assignments have been reported⁵ for one pair of geometric fulgide isomers. In the present paper, spectroscopic methods for structural assignments are extended to three more pairs of isomers. The three fulgides studied are α,α' -diveratrylidenesuccinic anhydride (diveratryl fulgide, I), α,α' -di(acetylguajacylidene)succinic anhydride (II) and α,α' -di(methoxymethylguajacylidene)succinic anhydride (III) (Fig. 1).

The study of *cis-trans* isomerism is complicated by further photoreactions, especially the facile oxidative cyclization to 1-arylnaphthalene derivatives.^{6,7}

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*Fig. 1.*

To suppress these reactions the benzene solutions of the fulgides were irradiated in a nitrogen atmosphere. On evaporation of the solutions and recrystallization of the residues, a more intensely coloured, crystalline product was obtained in all three cases. The photoisomers of (I) and (III) had a higher melting point than the starting material.

*Fig. 2.* NMR spectrum of diveratryl fulgide (I) in CDCl₃ with TMS as internal standard.*Fig. 3.* NMR spectrum of the photoisomer of I in CDCl₃ with TMS as internal standard.

The NMR spectra of substance (I) and its photoisomer are shown in Figs. 2 and 3. In the spectrum of the starting material (Fig. 2), the lowest field signal is due to the vinyl protons. In the spectrum of the photoisomer (Fig. 3) this signal occurs at still lower field and shows signs of splitting. The vinyl proton signals are similar in the other spectra. The results are summarized in Table 1. The single sharp signal from the vinyl protons and the simple pattern of signals from the aromatic protons indicate that the molecule of the starting material is symmetrical⁵ as shown in Fig. 1 for the structures Ia, IIa, and IIIa. In accordance with the nomenclature for diphenylbutadienes, this structure

Table 1. The chemical shifts of the vinyl proton signals for the three pairs of photoisomeric fulgides.

Substance	Vinyl proton signal (δ)	$\Delta \delta$
Ia	7.80	0.42
Ib	8.22	
IIa	7.90	0.31
IIb	8.21	
IIIa	7.83	0.45
IIIb	8.28	

is called *trans-trans*.⁵ Two structures, the *cis-trans* and the *cis-cis*, can be visualized for the photoisomer. Structural models (Dreiding) show that the *cis-cis* configuration is too crowded to be a probable stable form.* This leaves the *cis-trans* configurations shown in Fig. 1 for (Ib), (IIb), and (IIIb). The Dreiding models show further that the *trans-trans* isomer can assume an almost planar conformation, whereas there is considerable steric hindrance to coplanarity in the *cis-trans* isomer. The observed down-field shift of the vinyl proton signals in the NMR spectra can thus be accounted for on the basis of decreased conjugation in the fulgide molecule. To get a rough theoretical estimate of this effect, the π -electron charge densities at the carbon atoms bearing the vinyl hydrogen atoms were calculated by the Hückel molecular orbital method. In aromatic systems, good correlations have been obtained between the charge densities at carbon atoms and the NMR signals from the corresponding hydrogen atoms.⁸ Owing to limitations imposed by the computer

Table 2. The C=O stretching vibrations of the anhydride groups observed in the infrared spectra of the photoisomeric fulgides.

Substance	C=O bands (cm^{-1})		Difference (cm^{-1})
	<i>trans-trans</i>	<i>cis-trans</i>	
I	1812	1790	22
	1760	1748	12
II	1820	1793	22
	1780	1770	10
III	1812	1790	22
	1766	1745	21

* Note added in proof: In a recent article a different opinion in this matter has been expressed by Heller, H. G. and Swinney, B. in *J. Chem. Soc. C* 1967 2452.

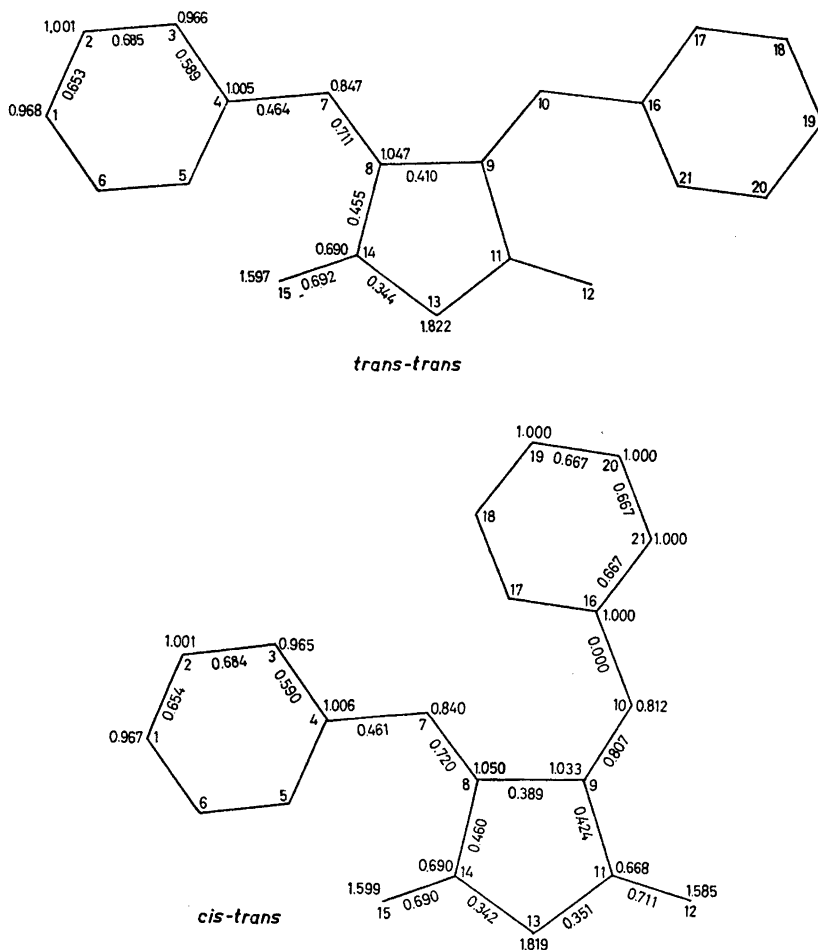


Fig. 4. Electron densities and bond orders obtained by the Hückel molecular orbital method for *trans-trans* and *cis-trans* dibenzylidene succinic anhydride.

programme, the aromatic substituents were ignored in the calculations. The heteroparameters were those listed by Streitwieser⁹ (see Experimental). To simulate the steric hindrance to coplanarity in the *cis-trans* isomer, the resonance integral between carbon atoms 10 and 16 (Fig. 4) was put equal to zero. Fig. 4 shows the bond orders and π -electron densities (q) obtained from the computer. The charge densities ($1-q$) on the carbon atoms 7 and 10 are plotted against chemical shifts from tetramethylsilane (δ) for the corresponding vinyl protons in Fig. 5, together with some values obtained by Forsén, Åkermark and Alm⁸ and the straight line obtained by them. The points for the *trans-trans* isomer lie in the vicinity of the line, which is notable in view of the

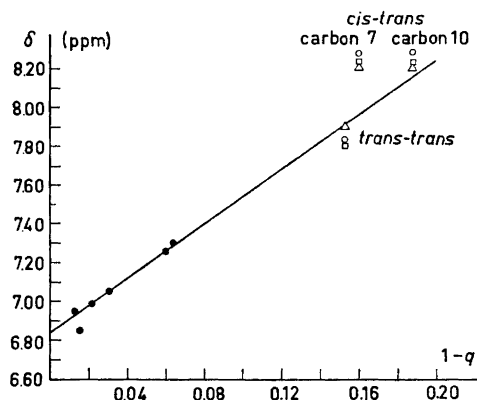


Fig. 5. The correlation between observed proton shifts (δ) and the calculated π -electron charge densities. Points marked ● and the straight line are from Ref. 8. The points marked □ are the values for I, Δ values for II and ○ values for III.

drastic approximations that were made, for the substituents on the aromatic rings were ignored as were also the differences in bond length between the aromatic and the butadiene systems. The calculated *cis-trans* model predicts a much larger difference in chemical shift between the vinyl protons at carbons

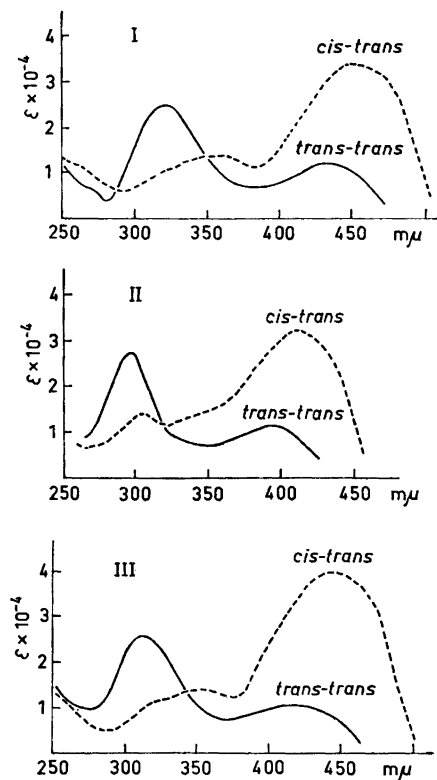


Fig. 6. Ultraviolet spectra of the three pairs of photoisomeric fulgides. (Solid line *trans-trans*, dotted line *cis-trans*).

7 and 10 than is actually observed. The conjugation is obviously not completely suppressed in the *cis-trans* fulgide as was assumed in the calculations. The mean value of the charge densities at carbons 7 and 10 predicts a smaller chemical shift than the observed one (predicted $\Delta \delta$ ca. 0.17, observed $\Delta \delta$ ca. 0.40 ppm). As a rough approximation, however, the results can be said to support the structural assignments shown in Fig. 1.

Some regularities were observed in the differences in the infrared and ultraviolet spectra of pairs of isomers. The two carbonyl bands typical of anhydrides¹⁰ occur at lower wavenumbers in the infrared spectrum of the *cis-trans* isomer than in the spectrum of the *trans-trans* isomer. The shift is of the same order of magnitude for all three pairs of isomers as shown in Table 2. The ultraviolet spectra are shown in Fig. 6. In all three cases the *cis-trans* isomers have an absorption maximum around 310 $m\mu$ the intensity of which is approximately half the intensity of the corresponding band of the *trans-trans* isomer. A similar effect has been observed for the sterically more hindered *cis* forms of cinnamic acids.¹¹ The deeper colour of the *cis-trans* fulgide is due to the intense absorbance around 450 $m\mu$, the cause of which is unknown.

EXPERIMENTAL

All melting points are corrected. The microanalyses were performed by A. Bernhardt, Mülheim, West Germany.

The *NMR spectra* were run with the compound dissolved in deuteriochloroform containing tetramethylsilane as internal standard on a Varian A 60 spectrometer by Techn. Lic. A. Klemola of the Finnish Institute of Technology, Otaniemi.

The *infrared spectra* were run on a Perkin-Elmer 537 apparatus using KBr wafers.

The *ultraviolet spectra* were recorded for 10^{-5} M solutions in chloroform on a Beckmann DB spectrometer using 1 cm quartz cells. The *syntheses* of the three fulgides (Ia, IIa and IIIa) have been described elsewhere.⁹

The *irradiations* were performed after dissolving ca 300 mg of the fulgide in 300 ml of benzene, heating the solution to the boiling point and cooling it in a stream of nitrogen. A high-pressure mercury lamp (S81, Quarzlampengesellschaft Hanau) in a water-cooled well made of Pyrex glass was inserted into the solution, which was irradiated for 1–2 h under nitrogen. The solution was evaporated to dryness and the residue recrystallized repeatedly from ethyl acetate and toluene. The yields of recrystallized product were ca. 30 %.

cis,trans- α,α' -Diveratrylidene succinic anhydride (Ib). Substance (Ia), m.p. 167–168° (dark red crystals), yielded brown-red crystals, m.p. 213–215°, on recrystallization from ethyl acetate. (Found: C 66.21; H 5.12. Calc. for $C_{22}H_{20}O_7$: C 66.68; H 5.09).

cis,trans- α,α' -Di(acetylguajacylidene) succinic anhydride (IIb). Substance IIa, m.p. 203° (bright yellow powder), yielded golden leaves melting at 198–200° (ethyl acetate). (Found: C 63.26; H 4.66. Calc. for $C_{24}H_{20}O_8$: C 63.71; H 4.42). The starting material (IIa) is phototropic;¹² the solid substance turns brown-red in sunlight in a few seconds. The original yellow colour returns on heating or recrystallization. The *cis-trans* isomer does not behave in this way.

cis,trans- α,α' -Di(methoxymethylguajacylidene) succinic anhydride (IIIb). (IIIa), m.p. 154–155° (orange crystals) yielded red crystals, m.p. 165–166° (toluene). (Found: C 63.01; H 5.38. Calc. for $C_{24}H_{24}O_9$: C 63.15; H 5.30).

The HMO calculations were carried out on an IBM 1620 computer at the Department of Applied Mathematics. The computer program used gave as output in addition to the eigenvalues and eigenvectors also the electron density-bond order matrix. The heteroparameters used were those listed by Streitwieser:⁹

$$\begin{array}{ll} \alpha_{C-O} = \alpha + 2\beta; & \alpha_{C=O} = \alpha + \beta \\ \beta_{C-O} = 0.8\beta; & \beta_{C=O} = \beta \end{array}$$

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