Photoreactions of 2,6-Diphenyl-s-Hydrindacene-1,3,5,7-Tetrone and its Derivatives in Polar and Nonpolar Solvents

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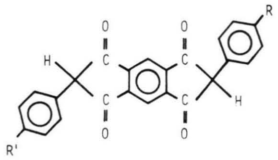
Continuous UV-irradiation as well as flash-photolysis of derivatives of 2,6-diphenyl-s-hydrindacene-1,3,5,7-tetrone (bisindandione – BID), substituted in the p and p′ positions of the phenyl rings, was found to result in the formation of stable photoproducts, of which the absorption, emission and excitation maxima coincide with those of the corresponding diarylidene-benzodifurandiones (bis-benzylidenephthalides – BBPh). Studies of light intensity effects gave evidence that this isomerization proceeds via a semi-isomerized intermediate. Additionally, flash-photolysis of BID showed the formation of short lived transients, which, however, are not the precursors of the stable photoproducts. These transients were assigned to 2,6-diphenyl-s-hydrindacene-1,3,5,7-tetrone-2-yl free radicals. Their UV-absorption maxima are dependent on the polarity of the solvent and show a bathochromic shift upon substitution.

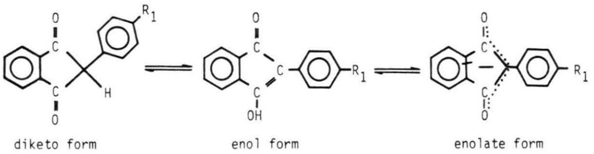
1. Introduction

The derivatives of 2,6-diphenyl-s-hydrindacene-1,3,5,7-tetrone (bisindandione – BID, see formula 1) are low molecular weight organic compounds with semiconductor properties [1]. However, up to now very little is known about their photochemical behaviour.



Formula 1. 2,6-diphenyl-s-hydrindacene-1,3,5,7-tetrone (bisindandione; BID).

In previous papers [2, 3] the photochemical properties of a number of derivatives of 2-phenylindan-1,3-dione (ID), substituted in the p-position of the phenyl ring were investigated. These compounds may exist in two tautomeric forms: the keto (K) and the enol (E) form. The quilibrium between these two forms depends on the polarity of the solvent, but even in highly polar solvents (95% ethanol) the K-form may be observed [4]. In alkaline solutions an enolate form is formed.



Formula 2. Equilibria of 1,3-indandiones.

Two independent photoreactions of ID have been observed: 1) Photorearrangement to 3-methylphenylene-1-(3H)-isobenzofuranones (also denoted as benzylidenephthalides), most likely via a Norrish type I mechanism) [2]. 2) Formation of short lived intermediates which were assigned to 2-arylindan-1,3-dion-2-yl free radicals [2, 3]. These processes take place both in polar and in nonpolar solvents. Despite a marked solvent dependence of the relative yields of the two pathways (isomerization is predominant in nonpolar solvents, free radical formation in polar solvents) it was not possible to elucidate clearly the specific role of the two tautomeric forms for the two photoprocesses.

The bisindandiones (see formula 1), which are the topic of the present study are principally ex-

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pected to exhibit photochemical properties similar to those of the indandiones. A previous study [5] showed that in contrast to ID the keto-enol equilibrium of BID is markedly shifted towards the E-form, even in nonpolar aprotic solvents (e.g. dichlorethane, dioxane). In polar protic solvents as ethanol BID exists almost exclusively in the enol-form. These compounds were therefore expected to be appropriate for studying the specific contribution of the enol-form for the photoreactions.

Because of the insolubility of the BIDs in nonpolar solvents, e.g. such as cyclohexane or n-heptane [5], dichlorethane, dioxane and ethanol were choosen as solvents.

2. Experimental

The investigated compounds given in Table 1 were synthesized by condensation of pyromellithic dianhydride with substituted phenylacetic acid [6, 7, 8] and subsequent treatment with sodium methylate [9, 10]. The resulting products were repeatedly recrystallized from glacial acetic acid until a constant melting point was obtained. Their purity was furthermore controlled by thin layer chromatography (mobile phases: $CH_3COOC_2H_5$: petrol ether = 4 : 1, $CH_3OH : CH_3COCH_3 = 3 : 1$, $CH_3OH : CHCl_3 = 1 : 1$; silicagel).

The used solvents were of fluorescence or reagent grade purity.

In order to avoid the formation of dimers of the starting compound [5] the concentrations of the solutions were kept below 10^{-5} dm^3 mol^{-1}.

The flash photolysis experiments were performed independently on two equipments: a) Flash Kinetic Spectrophotometer, KN 100 (Applied Photophysics, London) and b) modified apparatus "Northern Precision" as described elsewhere [2].

Fluorescence spectra were recorded by means of a spectrofluorimeter Perkin Elmer MPF 44B, absorption spectra on a Specord M40 (Carl Zeiss, Jena) or on a Hitachi 115-20 spectrophotometer. For the steady state photochemical experiments a medium pressure mercury lamp (Tungsram HGO 125 W) in connection with 1 cm spectrophotometric quartz cells was used.

In some experiments, flash irradiated solution was transferred to the spectrofluorimeter in order to confirm the formation of fluorescent products of the photoisomerization process.

Table 1. Investigated compounds.

Compound No.	Substituents (R, R_1)	Melting p. (°C)	Lit.
BID-1	H, H	305–307	[9, 11]
BID-2	CH_3, CH_3	306	[10]
BID-3	OCH_3, OCH_3	310–315	[11]
BID-4	H, OCH_3	296–300	[10]
BID-5	CH_3, OCH_3	318	[10]

3. Results

Flash photolysis of BID-derivatives in ethanol resulted in the formation of transients, similar to those of the corresponding ID-derivatives (see Table 2). However, a bathochromic shift of about 30 nm was observed. These transients decayed according to second order reactions (dimerization/disproportionation; $2k/\varepsilon = 10^6$ cm s^{-1}). The derivative with $R = H$ and $R_1 = OCH_3$ yields two transient peaks with maxima at the same wavelength as the individual symmetrically substituted compounds (see Figure 1). Because of the similar position of the transient maxima from BID 2 and BID 3 these two peaks coincide with BID 5 (See Table 2). With the solvent ethanol no formation of stable products was observed in the investigated wavelength region (330–800 nm).

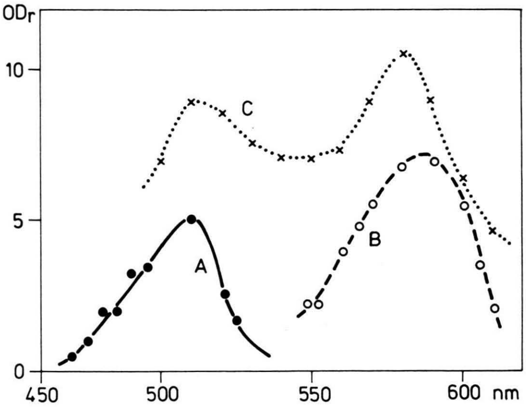


Fig. 1. Absorption spectra of transients formed by flash photolysis of bisindandione derivatives in ethanol, 10^{-5} mol dm^{-3}, purged with argon (discharge voltage 13 KV; 500 µs after flash. Curve A: BID-1 (H, H); curve B: BID-3 (OCH_3, OCH_3); curve C: BID-4 (OCH_3, H).

Table 2. Measured absorption maxima of transients obtained by flash photolysis of BID-derivatives in deoxygenated dichloroethane, ethanol and 1,4-dioxane.

Compound No.	Substituents (R, R_1)	λ_{max} observed in:			λ_{max} of the corresponding
		Dichloro-ethane	Ethanol	1,4-dioxane	ID-radicals in ethanol
BID-1	H, H	500	510	500	345, 540 [3] 510, [12]
BID-2	CH_3, CH_3	550	560	–	350, 540 [3]
BID-3	OCH_3, OCH_3	570	580	570	380, 550 [2, 3]
BID-4	H, OCH_3	500, 570	510, 550	–	–
BID-5	CH_3, OCH_3	380, 560	350, 570	–	–

Table 3. Absorption and fluorescence maxima of stable products obtained by stationary uv-irradiation and by flash photolysis of BID-derivatives in deoxygenated dichloroethane and 1,4-dioxane.

Compound No.	Substituents (R, R_1)	Dichloroethane				1,4-dioxane	
		Stat. irr.		Flash irr.		Flash irr. Abs.	uv-abs. of BBPh isomers
		Abs. (nm)	Fluor. (nm)	Abs. (nm)	Fluor. (nm)	(nm)	(nm)
BID-1	H, H	330 390	500	355 410 sh	500	355	355–350 390–410 (sh) [7, 8]
BID-2	CH_3, CH_3	340 390	510	390	510	–	–
BID-3	OCH_3, OCH_3	350 390	540	390	540	355 390	–
BID-4	H, OCH_3	330 400	530	390	530	–	–
BID-5	CH_3, OCH_3	–	–	390	–	–	–

In dichloroethane besides the formation of transients, stable products were also observed (see Table 3). A slightly different shape of the absorption band was observed at low flash intensities. When applying more than one low intensity flash to the same solution of H,H-BID, the rise of a shoulder at 410 nm was observed (see Figure 2).

Very similar results as found in dichloroethane were also obtained in 1,4-dioxane (see Tables 2, 3).

Under all conditions both, transients and final products, were found to be formed within the resolution time of the flash apparatus (< 50 μs).

Absorption and fluorescence maxima as obtained under stationary conditions (Table 3) agree well with the stable absorptions obtained in the flash experiments.

4. Discussion

The keto-enol tautomeric equilibrium of the BID-derivatives in solution is always strongly shifted to the enol form, in contrast to the ID-compounds, which even in alcohol solutions are to a certain extent in the diketo-form [5]. This equilibrium is also affected by the formation of dimers [5]. In the present study the concentrations were therefore kept below the limit of dimerization (10^{-5} mol dm^{-3}).

The results given evidence for principally similar BID-photoreactions as found with the ID-compounds [2, 3], namely the formation of stable products (absorbing in the region 250–410 nm, fluorescing at ≅ 500 nm) and of short lived transients ($\lambda_{max} \cong 500-600$ nm), which are not the precursors of these final products.

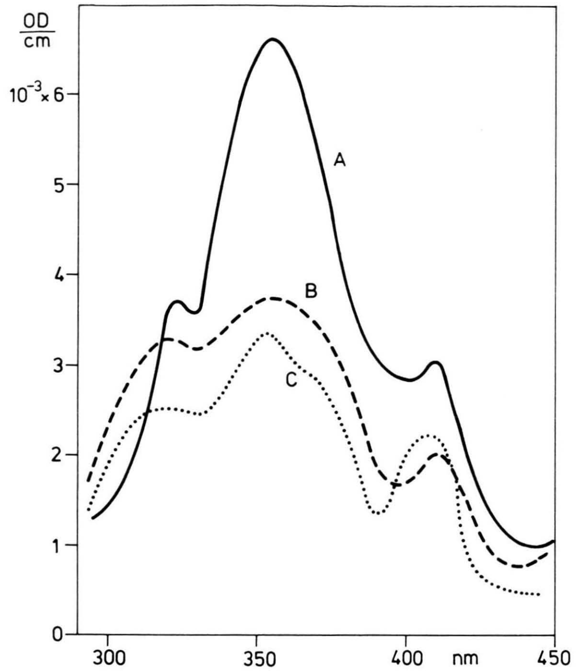


Fig. 2. Absorption spectra of products formed by flash photolysis of BID-1 in ethanol, 10^{-5} mol dm^{-3}, purged with argon (discharge voltage 6 kV; 1 s after flash. Curve A: 1 flash applied to solution; curve B: 3 flashes; curve C: 6 flashes.

The absorption maxima of the transients correspond to those which are obtained with the ID-derivatives with the corresponding substituents, but are bathochromically shifted for ca. 30 nm (see Table 2). The spectra obtained with unsymmetrically substituted compounds represent a combination of the maxima of the absorptions of the two symmetrically substituted compounds.

Substituent and solvent effects are principally similar as previously obtained with the ID-derivatives [3, 13, 14], but the data at disposal are not sufficient for a systematical investigation of these effects. These results strongly suggest to assign an indandionyl free radical structure to the observed transients.

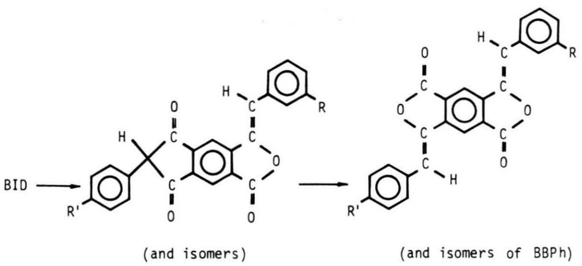
The formation of radicals in dichloroethane as well as in ethanol gives strong evidence for their generation via splitting of the O−H bond of the enolform. As the enol form is present in all solvents, it cannot be decided whether the diketo-form may split at the C−H bond in α-position to both C=O groups.

The decay of the transients follows a typical second order reaction (dimerization/disproportionation). The exact values of the transient's extinction coefficient (ε) are not known. However, an approximate value of 6×10^4 dm^3 mol^{-1} cm^{-1} has been measured [15] for the monoindandionyl free radicals. Therefore, assuming $\varepsilon \cong 10^4$ dm^3 mol^{-1} cm^{-1}, an absolute rate constant of $2k \cong 10^{10}$ dm^3 mol^{-1} s^{-1} can be estimated in dichloroethane, which corresponds approximately to the diffusional limit.

The final products to be expected as a result of dimerization have the same chromophore as the starting compound and are therefore not detectable without chemical separation.

In analogy to indandione and other β-diketones [2, 3, 16, 17] a splitting according to a Norrish type I reaction with subsequent isomerization to arylidenisobenzofuranones (benzylidenephthalides, BPh) and diarylidenebenzodifurandiones (bisbenzylidenephthalides, BBPh) is likely to occur. Absorption and emission spectra of BBPh derivatives have been reported previously [7, 8]. They may exist in six geometrical isomers (eight for unsymmetrically substituted compounds). The isomers of unsubstituted BBPh show strong absorption bands at ca. 335–350 nm with a characteristic shoulder at ca. 390–410 nm [7, 8]; fluorescence emissions are between 500 and 550 nm [7]. These spectral data are in good agreement with the obtained results.

Absorption and emission spectra of BID-isomerized in one moiety of the molecule to phthalid are not known. Its chromophore, however, corresponds to that of 5,6-dicarboxy-3-phenylmethyleneisobenzofuranone and to that of its anhydride. Their absorption maxima in 1,4-dioxane are between 350 and 395 nm [18, 19], i.e. in the same spectral region as the BBPh.



Formula 3. Two steps photoisomerization of BID.

The formation of BBPh as products of stationary irradiation and flash photolysis at high intensities of

BID in dichlorethane and 1,4-dioxane was demonstrated both by absorption and fluorescence spectroscopy. Work about the distribution of geometrical isomers is in progress. Experiments at low flash intensity showed the gradual increase of a shoulder at 410 nm (characteristic for the BBPh) when more flashes were applied to the same solution. This suggests the formation of BBPh in a two photon process via an intermediate, which is isomerized in one moiety of the molecule (see formula 3).

The absence of BBPh products in ethanol (tautomeric equilibrium shifted totally to the enol-form) gives strong evidence for the photoisomerization to proceed via the diketo-form and confirms, furthermore, the assumed pathway via a Norrish type I reaction. It is likely to lead to an intermediate, which is too short-lived to be observed within the time resolution of our flash apparatuses. For the ID-derivatives this could not be shown so clearly, because in this case even in ethanol some amounts of the diketo-form are present. A strong wavelength effect has been observed for the photoisomerization of ID- to BPh-derivatives, showing a negligible isomerization quantum yield at long wavelengths in ethanol. As in this wavelength region only the enol-form is absorbing, evidently the isomerization of the indandione derivatives originates from their diketo-form only.

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