Absorption Spectra of Substituted 2-Phenylindan-1,3-Dion-2-YL Radicals in Solution

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Flash photolysis of a series of 2-phenylindandione-1,3 derivatives substituted in the 4′ position results in both the formation of stable benzylidenephthalides and of phenylindan-1,3-dion-2-yl radicals. The u.v. absorption maxima of these radicals are dependent on the solvent and show a bathochromic shift upon substitution. These substitution effects were correlated by means of a linear free energy relationship. Attempts were made to draw conclusions concerning the changes in the gap of the states involved and their curvature due to substitution.

1. Introduction

Free radicals derived from arylindandiones are of significant importance in several processes of technological interest [1]. They may be formed by chemical oxidation [2], photolysis of the corresponding indandiones [3] or by photolysis [4], respectively thermolysis [5] of the 2-2′ indandione dimer.

In a previous study [6] it was found that upon u.v. irradiation of derivatives of 2-phenylindandione-1,3 in different solvents a cleavage of the H-atom in α-position to both keto groups occurs, under formation of the corresponding radicals. These radicals react in almost diffusion controlled dimerization reactions [4, 7]. In addition to this a photoisomerisation process to benzylidenephthalides is observed, most likely after bond splitting due to a "Norrish type I" mechanism. Both processes are observed from the diketoform (in apolar solvents) as well as from the enolform (in alcohols) and from the enolate form (in alkaline water) with different yields, however.

The purpose of the present work was to investigate in more detail the occurrence of these processes with a greater number of derivatives of 2-phenylindandione-1,3 and to pay special attention to the spectroscopic properties of the radicals formed. In addition to the reported solvent effects on the spectra of the 2-(4′-dimethylaminophenyl)-indan-1,3-dion-2-yl radical [5] and to the results concerning the substituent effects on the absorption spectra for some derivatives [3] it was of particular interest to study also the substituent effects using a larger series of derivatives substituted in the 4′-position. An attempt has been made also to perform a detailed analysis applying a linear free energy relationship [8].

2. Experimental part

The absorption spectra of the free radicals were taken by flash photolysis of the corresponding 2-phenylindandione derivatives in argon saturated solutions. A list of the compounds and references for their synthesis are given in Table 1. All substances purified by recrystallization and were found to be homogeneous in t.l.c. tests. Other chemicals were R.G. quality (E. Merck, Darmstadt). Water was distilled four times. Before use the solutions were deoxygenated by purging with argon. The flash photolysis experiments were performed independently on two equipments (Applied Photophysics, London, and a modified apparatus "Northern Precision"), which are described elsewhere [6].

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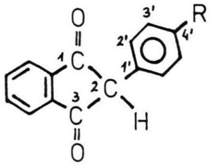
Table 1. List of investigated compounds.

Substance	Substituent (*R*)	Ref. of Synthesis
I	$-N(CH_3)_2$	[9]
II	$-NH_2$	[9]
III	$-NHCOCH_3$	[9]
IV	$-OCH_3$	[10, 11]
V	$-CH_3$	[10, 11]
VI	$-F$	[12]
VII	$-Cl$	[12]
VIII	$-H$	[12]
IX	$-CN$	[13]
X	$-Br$	[12]



3. Results

In all the investigated solvents (cyclohexane, ethanol, alkaline water at pH = 12) generally the formation of stable product and of a transient were observed. In Fig. 1 the absorption spectra of the transients and of the stable product are shown for compounds (II), (III) and (VIII) in ethanol. Further spectrosopic data are compiled in Tables 2–4. Generally the highest radical yields were observed in apolar solvents and with donor substituted derivatives.

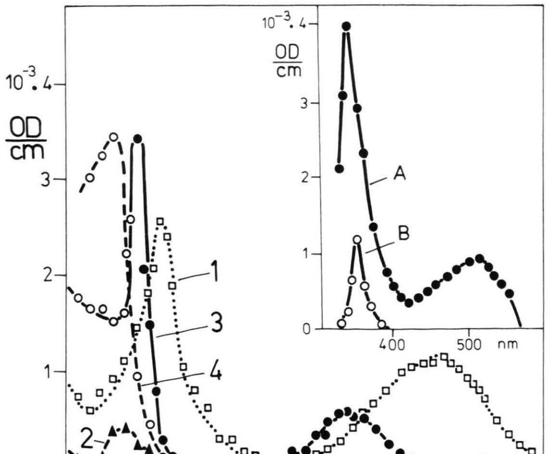


Fig. 1. Absorption spectra obtained by flash photolysis (discharge voltage 12 kV) of deoxygenated ethanolic solutions of 2×10^{-5} mol · dm^{-3} 2-phenylindandione-1,3 derivatives. 1) (II) (4′-amino) transient 200 µs after flash; 2) (II) stable product; 3) (III) (4′-acetylamino) transient 200 µs after flash; 4) (III) stable product. Insert: (A) (VIII) (unsubstituted) transient 200 µs after flash, B) (VIII) stable product.

The absorption spectra of the stable products obtained by flash photolysis agree well with those of the benzylidenphthalides having the same substituents in the phenyl ring [15] (Table 3). In aqueous alkaline solution (pH = 12) of the formation of the benzylidenephthalides was observed only for compounds (I), (II) and (III) (Table 4) and even then with small yields only.

The transients decay according to second order kinetics. For 2-(4′-dimethylaminophenyl)-indan-1,3-dion-2-yl radicals in ethanol at 735 nm a value of $k_2/\varepsilon = 1.2 \times 10^5$ cm · s^{-1} was obtained.

In addition longlived transients were observed in aqueous alkaline solution for the unsubstituted compound (VIII) and for the bromosubstituted compound (X). For (VIII), $\lambda_{max} = 630$ nm, $\tau/2 \cong 10$ ms and for (X), $\lambda_{max} = 380$, 660 nm, $\tau/2 \cong 10$ ms were found.

Table 2. Absorption maxima of stable products and of transients as obtained by flash photolysis of 2-phenylindandione-1,3 derivatives in deoxygenated cyclohexane.

Substance	Substituent (*R*)	Absorption maximum (λ_{max}, nm) of: Stable Product	Transient
I	$-N(CH_3)_2$	390	420, 610, 670
II	$-NH_2$	370	350
III	$-NHCOCH_3$	325	350
IV	$-OCH_3$	340	–
IX	$-CN$	325	340

Table 3. Absorption maxima of stable products and of transients obtained by flash photolysis of 2-phenylindandione-1,3 derivatives in deoxygenated ethanolic solutions as well as of benzylidenephthalides with same substituent in the benzene ring.

Substance	Substituent (*R*)	λ_{max} of Phthalid [14]	Absorption maxima (λ_{max}, nm) of: Stable Product	Transient
I	$-N(CH_3)_2$	395	390	430, 660, 735
II	$-NH_2$	–	390	420, 660
III	$-NHCOCH_3$	373	380	400, 575
IV	$-OCH_3$	356	360	380, 550
V	$-CH_3$	356	350	350, 540
VI	$-F$	–	–	380, 530
VII	$-Cl$	372	370	365, 520
VIII	$-H$	338	320	345, 540
IX	$-CN$	342	320	345, 540
X	$-Br$	–	365	370, 540

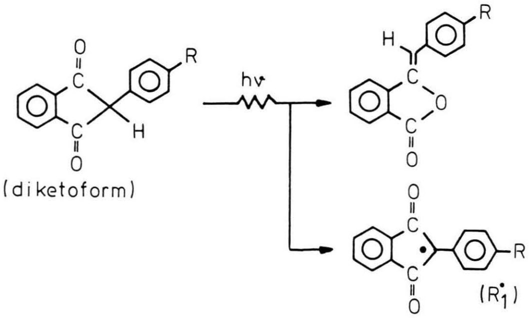
Table 4. Absorption maxima of stable products and of transients obtained by flash photolysis of 2-phenyl-indandione-1,3 derivatives in deoxygenated aqueous solutions (pH = 12).

Substance	Substituent (*R*)	Absorption maxima (λ_{max}, nm) of:	
		Stable Product	Transient
I	$-N(CH_3)_2$	390	410, 670, 750
II	$-NH_2$	390	410, 670
III	$-NHCOCH_3$	400	390, 610
IV	$-OCH_3$	–	380, 585
VIII	–H	–	< 460, 530
X	–Br	–	< 360, 555

The long wavelength band of the radical derived from (I) appeared as a double peak in all the three solvents investigated; it did not appear with the other derivatives.

4. Discussion

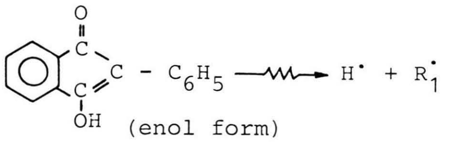
For the investigated derivatives the photochemical behaviour corresponds generally to that of (I) as reported previously [6]. On one hand the formation of a stable product was observed, which was fond to be benzylidenephthalide [15], whereas on the other hand a one electron photooxidation process yields a 2-arylindandion-2-yl radical which dimerizes in due course:



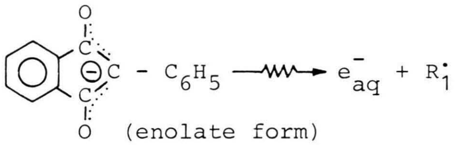
(1)

(2)

In addition to reaction (2) the indandionyl radicals can also be formed from the enol form by splitting of the O–H bond (reaction 3) or from the corresponding enolate from by photoejection of a solvated electron (e_{aq}^-; reaction 4):



(3)



(4)

The photoisomerisation of the substrate to benzylidenephthalides (reaction 1) is most likely accomplished by a C1–C2 bond splitting (Norrish Type I mechanism) leading to a very shortlived biradical which leads the phthalide after rotation around a C–C single bond [6]. Within the resolution time of our flash photolysis apparatus ($\tau/2 \cong 7\,\mu s$) it was not possible to detect shorter lived triplet states or other precursors of the indandionylradicals or benzylidenephthalides.

Both processes, radical formation and electron ejection, are possible from the diketoform (in apolar solvents) as well as from the enolform (in alcohols) and from the enolate form (in alkaline water). The yields of the free radicals (reaction 2) are highest in alkaline water, those of phthalide (reaction 1) in apolar solvents. In alkaline solutions phthalides are formed with electron donor substituted compounds only and even then in small yields. Up to now it was not possible to assign the longlived transient bands formed at flash photolysis of substances (VIII) and (X).

The absorption spectra of 2-arylindandion-2-yl radicals show a pronounced solvent dependence (Tables 2 to 4). They are shifted bathochromatically in solvents with higher dielectric constants. An analysis of the solvent effects on the radical derived from (I) by means of the Bakshiev equation [16] indicated a strong charge transfer character of the free radical's excited state (a higher dipole moment than in the ground state) [5]. Our results in cyclohexane, ethanol and water principally confirm these findings, moreover, they show that all radicals with electron acceptor substituents exhibit an analogeous solvent effect, indicating an excited state with charge transfer character.

Apart from this solvent influence the derivatives investigated in the present work are characterized by a substituent effect with respect to the spectral position of its absorption bands. In Fig. 2 correlation diagrams, according to the Hammett equations (3) and (4) are shown:

$$\Delta\nu_{abs} = \varrho_{abs}\cdot\sigma_p + C\,, \tag{3}$$

$$\Delta\nu_{0\text{-}0} = \varrho_{00}\cdot\sigma_p + C\,. \tag{4}$$

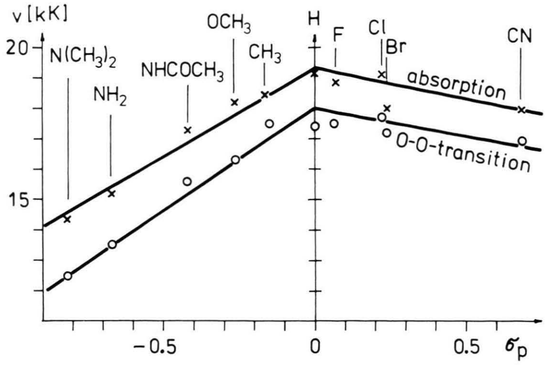


Fig. 2. Linear correlations of O–O transitions and absorption maxima for some substituted 2-phenylindan-1,3-dion-2-al free radicals in ethanol (see text). O–O transitions were estimated from long wavelength absorption edges, for the dimethylaminosubstituted derivatives the center of the double peak was taken as maximum.

Each diagram consists of two branches with $\varrho_{\text{abs}} = 6.20 \times 10^3\ \text{cm}^{-1}$ and $\varrho_{00} = 6.56 \times 10^3\ \text{cm}^{-1}$ for negative σ_p-values and $\varrho_{\text{abs}} = -1.74 \times 10^3\ \text{cm}^{-1}$ and $\varrho_{00} = -1.52 \times 10^3\ \text{cm}^{-1}$ for positive σ_p-values. For the positive branches the correlation is much worse, because of the limited amount of data. A similar shift of the absorption spectra is obtained in cyclohexane and in water, but in these cases the available data are not sufficient for the construction of linear correlation diagrams.

The correlations for the absorption maxima differ from a previous one [3], which found $\varrho_{\text{abs}} = 2.5 \times 10^4\ \text{cm}^{-1}$ for $\sigma < 0$ as well as for $\sigma > 0$. This is most likely due to the smaller set of derivatives, also including others than 4′-substituted compounds; furthermore due to the use of different solvents for the same correlation and finally because the authors [3] could not observe the long wavelength maximum of the 4′-bromosubstituted compound. For these reasons we suggest to keep to the correlations presented here rather than to the previous ones [3].

By means of a recently developed theoretical approach [8, 17] it is possible to use the linear correlations between spectral parameters and the Hammett σ-constants (Fig. 2) for separating the substituent effects on the Frack-Condon transitions into two independent components:

1) the influence on the energy gap between the ground state and the excited state.
2) the influence on the steepness of the hypersurfaces of these states.

The coefficient ϱ_{00} is related to the zero vibrational level energies of the ground and excited states as follows [8]:

$$\varrho_{00} = \frac{1}{h}\left[\left(\frac{\partial E_1^0}{\partial x}\right)_H - \left(\frac{\partial E_0^0}{\partial x}\right)_x\right], \tag{5}$$

where the partial differential quotients are a measure for the sensitivity of the two states involved to substitution. As in our case $\varrho_{00} < 0$ for $\sigma < 0$ and $\varrho_{00} > 0$ for $\sigma > 0$ the energy gap between ground and excited state is generally diminished upon substitution.

For the difference $\varrho_A - \varrho_{00}$ the following relation holds [8]:

$$\varkappa_1 = \varrho_{\text{abs}} - \varrho_{00} \cong \frac{1}{2h}(\vec{R}_1 - \vec{R}_2)^2 \cdot \left(\frac{\partial k_1}{\partial x}\right)_H . \tag{6}$$

The value of $\varkappa_1$ is determined by geometry changes $(\vec{R}_1 - \vec{R}_0)$ as well as by changes of the force constants upon substitution ($\partial k_1/\partial x$, which indicates the curvature of the excited states hypersurface). In our case both effects are obviously small. The slightly negative value of $\varkappa_1$ for $\sigma < 0$ indicates a slight increase in the steepness of the excited state's surface $\vec{E}_1(R)$ upon substitution with electron acceptor substituents.

Quantum chemical calculations on the excited state of 2-arylindandion-2-yl free radicals are in progress.

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[1] V. V. Moiseev and I. T. Poluektov, Usp. Khim. **42,** 471 (1973).
[2] F. Nathanson, Chem. Ber. **26,** 2576 (1893).
[3] A. I. Yasmenko, A. A. Kuznetsov, and I. V. Khudyakov, Zh. Fiz. Khim. **54,** 1776 (1980).
[4] I. V. Khudyakov, A. I. Yasmenko, and V. A. Kuzmin, Int. J. Chem. Kinet. **11,** 621 (1979).
[5] A. I. Yasmenko, A. P. Khardin, I. V. Khudyakov, and V. A. Kuzmin, Izv. Akad. Nauk SSSR, ser. khim. 2014 (1980).
[6] J. Zechner, G. I. Grabner, G. Köhler, N. Getoff, I. Timtcheva, F. Fratev, and St. Minchev, J. Photochem. **23,** 61 (1983).
[7] A. I. Yasmenko, I. V. Khudyakov, A. P. Darmanjan, V. A. Kuzmin, and S. Claesson, Chem. Scripta **18,** 49 (1981).
[8] O. E. Polansky, F. Fratev, and P. Nikolov, Z. Naturforsch. **36a,** 197 (1981).
[9] O. Neilands and M. Cirule, Latvijas PSR Zinatum Akademijas Vestis, Kim Ser. p. 65 (1963), in Russian.
[10] S. Shapiro, K. Geiger, J. Youlus, and L. Freedman, J. Org. Chem. **26,** 3580 (1961).
[11] P. Hrinciar, Acta Facult. rer. natur. Univ. Comenianae Chimia, **10,** 527 (1966).
[12] S. Shapiro, K. Geiger, and L. Freedman, J. Org. Chem. **25,** 1860 (1960).
[13] G. Gavallini, E. Milla, E. Grumelli, and F. Ravenna, Farmac. Ed. Sci. **10,** 710 (1955).
[14] P. Nikolov, F. Fratev, and St. Minchev, Z. Naturforsch. **38a,** 200 (1983).
[15] J. Rigaudy and P. Derible, Bull. Soc. Chim. France **1965,** p. 3047, 3055, 3061.
[16] N. G. Bakshiev, Opt. i Spektroskopiya **10,** 717 (1961).
[17] F. Fratev, P. Nikolov, and O. E. Polansky, Z. Naturforsch. **37a,** 1341 (1982).