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Photophysics of ambident organic anions I

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Abstract

The absorption and emission properties of saccharin, phthalimide, isatin and their anions were determined and analyzed. The conjugate bases of phthalimide and saccharin show parallel behaviour. The fluorescence occurrence is associated to an excited state with an electron-rich aromatic ring (including the example of anomalous emission). The lifetime in protic solvents is a function of the kind of the solute–solvent hydrogen bond mechanism. Alternative hydrolysis two steps mechanism is suggested for phthalimide and isatin in view of the observed photophysical behaviour.

Keywords: Saccharin photophysics; Phthalimide photophysics; Solvent effects; Ambident organic anions

1. Introduction

Preparative photochemistry employing organic anions (carbanions, nitranions and oxianions) is an emergent- and example-plenty research field which, before a complete behaviour generalization, struggles for a more definitive mechanistic description [1]. Among the intrinsic difficulties is the fact that the multiplicities of the photoreactions cannot be determined by the usual methods [1]. In addition, the properties of organic anions are influenced deeply by the nature of the solvent and cation in the ground and excited states [2]. Moreover, organic anion photochemistry is often dominated by electron ejection processes [3].

Reviews on anion photochemistry [4,5], illustrate these limitations. Photophysical studies are restricted to resonance stabilized anions in which photoejection is minimized. Nevertheless, in general (owing to the high substrate pKas) the studies are frequently carried out in apolar non-protic solvents where ion pairing is present.

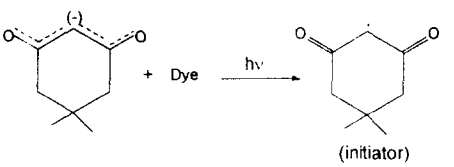
Tolbert [6] has suggested that it is possible to improve organic anion photophysics experiments by an appropriate choice of counter-ion and a convenient molecular structure design.

From ground state organic chemistry it is known that a carbanionic centre attached directly to a carbonyl or sulfonyl group exhibits greater stability [7]. However, photo-electron transfer would remain as an undesirable primary process [8]. Dimedon, an ambident carbonyl stabilized anion, has been employed as photoinitiator in the presence of an appropriate dye oxidant [9] (Scheme 1).

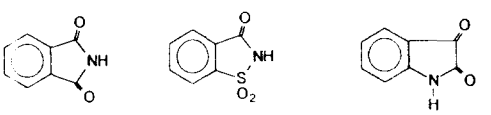
This work has in view the study of the photophysics of the class of aromatic organic anions carbonyl/sulfonyl stabilized designed to be examined in polar protic and aprotic solvents.

These requisites were met by the sodium salts [10] of the readily available conjugate bases of the aromatic heterocyclic systems bearing the functions: (a) imide (phthalimide); (b) 0-sulfobenzimide (saccharin) and (c) oxamide (isatin) (Scheme 2).

Fluorescence spectra, fluorescence quantum yields, fluorescence lifetimes and electronic absorption spectra of the organic ambident anions sodium phthalimide, sodium saccharinate and sodium isatin are determined. For comparison,



Scheme 1. Dimedon photoinitiator.



(a) Phthalimide b) Saccharin c) Isatin

Scheme 2. Formulae of the three parent heterocyclic systems.

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also investigated were the electronic spectra and emissive properties of the parent, conjugated acids (a, b and c).

2. Experimental details

Saccharin was synthesized by chlorosulfonation of toluene, followed by reaction with ammonium carbonate, oxidation with permanganate, and treatment with HCl [11]. Sodium saccharinate was prepared by the reaction of saccharin with NaOH in ethanolic solution [12,13]. Two recrystallizations from hot water were used to purify the salt. The N-alkyl derivatives (methyl, propyl) were prepared according to Rice and Pettit [14], reacting sodium saccharinate with the alkyl halides in DMF. Phthalimide (Merck) was recrystallized from ethanol. Sodium phthalimide was prepared from phthalimide following the literature procedure [15]. Isatin (Fluka) was recrystallized twice from water. Sodium isatin was prepared by the Arbuzov method [16]; isatin was treated with sodium ethoxide in absolute ethanol. Quinine bisulfate (QBS, Sigma) was recrystallized three times from dilute aqueous solutions of sulfuric acid [17]. All the synthesized products were identified on the basis of melting point, thin-layer chromatography, proton NMR and IR spectra. All aqueous solutions were prepared using Milli-Q water. Ethanol was distilled from KOH and acetonitrile from P_2O_5 [18]. Methanol, DMF and DMSO were spectroscopic grade. All other reagents were analytical grade. Absorption measurements were performed on a Hitachi U-2000 spectrophotometer. Corrected steady-state fluorescence spectra were recorded on an Edinburgh Instruments photon counting spectrofluorimeter. Fluorescence quantum yields were determined according to Parker and Rees [19], using QBS in 1.0N H_2SO_4 solution ($\phi = 0.546$ [17]) as fluorescence standard. Fluorescence decays were measured by single-photon timing, using an Edinburgh Instruments CD 900 time-resolved fluorimeter. Excitation was provided by a hydrogen-filled nanosecond flash lamp. The decay times were determined by using a recinvolution program based on the Marquardt algorithm for non-linear least squares. Standard deviations of the optimized parameters were calculated from the diagonal elements of the covariance matrix in the last iteration.

3. Results

3.1. Electronic absorption spectra

Saccharin, N-alkyl saccharin and sodium saccharinate

The absorption spectrum of saccharin, shown in Fig. 1, presents an intense absorption at 207 nm ($\epsilon \approx 27300\ M^{-1}\ cm^{-1}$) and shoulders at 224 nm ($\epsilon \approx 5900\ M^{-1}\ cm^{-1}$) along with a lower intensity band with two vibrational features at 276 nm ($\epsilon \approx 800\ M^{-1}\ cm^{-1}$) and 283 nm ($\epsilon \approx 600\ M^{-1}\ cm^{-1}$). The N-alkyl (methyl and propyl) saccharin derivatives have similar characteristics (data not shown), with maxima at 220 nm ($\epsilon \approx 18000\ M^{-1}\ cm^{-1}$) and at 269 nm ($\epsilon \approx 800\ M^{-1}\ cm^{-1}$).

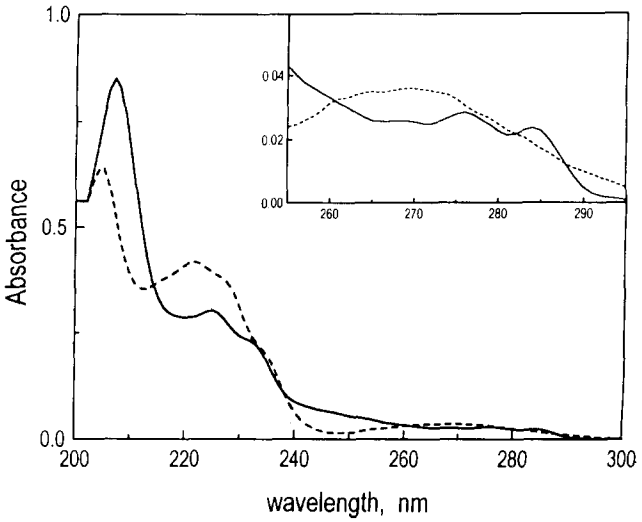


Fig. 1. Absorbance spectra of saccharin 3.8×10^{-5} M (——) and sodium saccharinate 3.3×10^{-5} M (– – –) in ethanol. Insert: blow-up of the 250–300 nm region.

Sodium saccharinate in ethanolic solution, Fig. 1, shows an intense band at 204 nm ($\epsilon \approx 29100\ M^{-1}\ cm^{-1}$); medium intensity bands at 220 nm ($\epsilon \approx 14600\ M^{-1}\ cm^{-1}$), 226 nm ($\epsilon \approx 12500\ M^{-1}\ cm^{-1}$) and 234 nm ($\epsilon \approx 6500\ M^{-1}\ cm^{-1}$), and a broad low intensity band centered at 270 nm ($\epsilon \approx 1000\ M^{-1}\ cm^{-1}$) with a lower wavelength vibrational structure at 283 nm ($\epsilon \approx 421\ M^{-1}\ cm^{-1}$). The usual bathochromic shift of the first absorption band of the anion compared with the corresponding neutral molecule [8] is not observed. However, the overall electronic spectra are affected by solvent; in polar aprotic media like HMPA, DMF and DMSO the saccharinate ion displays just one structureless band in the near ultraviolet region, with a maximum around 270 nm and $\epsilon \approx 1600\ M^{-1}\ cm^{-1}$ (data not shown).

3.2. Phthalimide, sodium phthalimide and phthalamic acid

The absorption spectra of phthalimide and its conjugate base, in ethanol, are shown in Fig. 2. Phthalimide has a high-intensity band at 217 nm ($\epsilon \approx 4000\ M^{-1}\ cm^{-1}$); medium intensity bands at 230 nm ($\epsilon \approx 10700\ M^{-1}\ cm^{-1}$) and 238 nm ($\epsilon \approx 10700\ M^{-1}\ cm^{-1}$); and a lower intensity band with two vibrational structures at 292 nm ($\epsilon \approx 1900\ M^{-1}\ cm^{-1}$) and 298 nm ($\epsilon \approx 1870\ M^{-1}\ cm^{-1}$) [20]. Sodium phthalimide exhibits bands at 210 nm ($\epsilon \approx 39900\ M^{-1}\ cm^{-1}$); 230 nm ($\epsilon \approx 18410\ M^{-1}\ cm^{-1}$), 238 nm ($\epsilon \approx 13550\ M^{-1}\ cm^{-1}$), and 247 nm ($\epsilon \approx 7700\ M^{-1}\ cm^{-1}$) and inflections at 289 nm ($\epsilon \approx 2762\ M^{-1}\ cm^{-1}$) and 300 nm ($\epsilon \approx 2300\ M^{-1}\ cm^{-1}$). In polar aprotic solvents, sodium phthalimide shows just one band, centered at 310 nm (data not shown).

Phthalamic acid (the final product of hydrolysis) has a maximum at 270 nm ($\epsilon \approx 1000\ M^{-1}\ cm^{-1}$), in agreement with the literature [21].

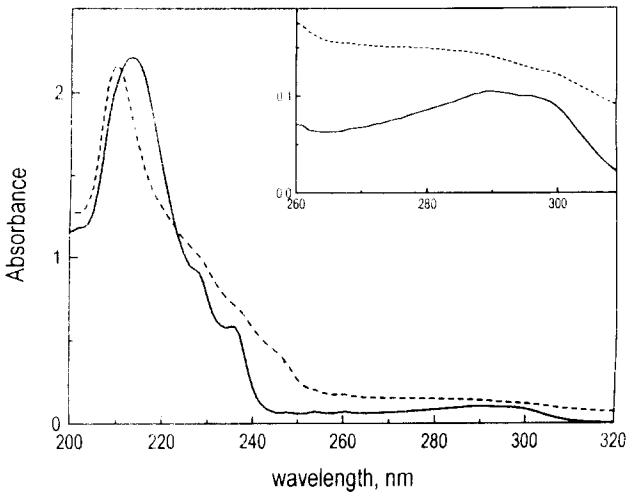


Fig. 2. Absorbance spectra of phthalimide 5×10^{-5} M (——) and sodium phthalimide 4.7×10^{-5} M (– – –) in ethanol. Insert: blow-up of the 260–320 nm region.

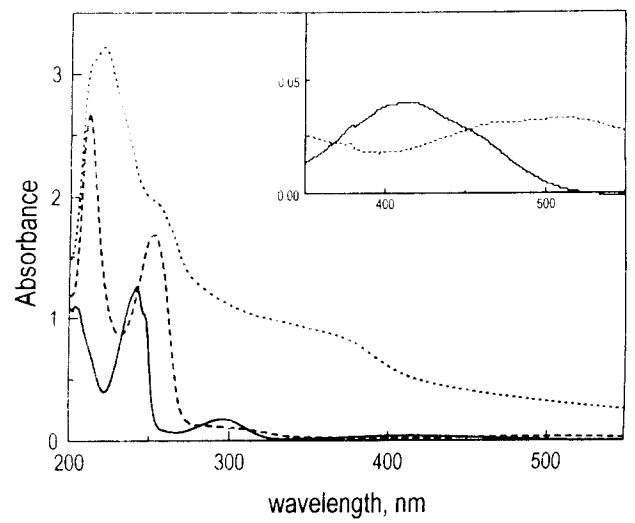


Fig. 3. Absorbance spectra of isatin (——), sodium isatin (– – –) and sodium isatate (· · · · · ·), all 7×10^{-5} M in ethanol. Insert: blow-up of the 350–550 nm region.

3.3. Isatin, sodium isatin and sodium isatate

The electronic spectra of isatin and its derivatives (sodium salt and hydrolysis product) are shown in Fig. 3.

Isatin exhibits four absorption bands in the near ultraviolet and visible regions, corresponding to electronic transitions of π, π^* and n, π^* character [22]. In ethanol, its absorption bands are located at 204 nm ($\epsilon\approx20500\ M^{-1}\ cm^{-1}$), 243 nm ($\epsilon\approx22374\ M^{-1}\ cm^{-1}$), 296 nm ($\epsilon\approx3160\ M^{-1}\ cm^{-1}$) and 420 nm ($\epsilon\approx750\ M^{-1}\ cm^{-1}$). The bathochromic shift experienced by the first absorption band with the increase of the solvent polarity has been ascribed to a certain charge–transfer character of this n, π^* transition [23].

Addition of isatin to an aqueous solution of NaOH yields a red–purple solution of the sodium salt which almost instantaneously gives place to a yellow solution owing to the formation of the hydrolysis product [24]. The addition of a small amount of the organic solvent to water decreases the rate of isatin hydrolysis by hydroxide [25]. Sodium isatin solutions in ethanol are stable [24]. The electronic absorption spectrum in absolute ethanol shows peaks at 211 nm ($\epsilon\approx47770\ M^{-1}\ cm^{-1}$), 251 nm ($\epsilon\approx30000\ M^{-1}\ cm^{-1}$), 300 nm ($\epsilon\approx1990\ M^{-1}\ cm^{-1}$) and 506 nm ($\epsilon\approx600\ M^{-1}\ cm^{-1}$). The longest wavelength band is red shifted in polar aprotic solvents [26].

The absorption spectrum of the yellow solution obtained by heating isatin or sodium isatin in alkaline alcohol solution exhibits peaks at 410 nm ($\epsilon\approx17800\ M^{-1}\ cm^{-1}$); 256 nm ($\epsilon\approx3500\ M^{-1}\ cm^{-1}$) and 367 nm ($\epsilon\approx2600\ M^{-1}\ cm^{-1}$) [27].

3.4. Fluorescence spectra

Sodium saccharinate fluorescence

No fluorescence emission could be detected for saccharin in any organic solvent used in the present work. A similar behaviour was found for N-alkyl saccharin solutions. In contrast to N-alkyl phthalimides [28,29], polar protic solvents do not induce fluorescence of the N-alkyl saccharin derivatives. In contrast, sodium saccharinate exhibited emission in all solvents, from water to cyclohexane.

Literature reports two previous studies of saccharin fluorescence. Brum [30], in a dermatologic study correlating fluorescence spectra and skin photosensitization, mentioned saccharin as a fluorescent molecule that emits at 450 nm in absolute ethanol when excited at 324 nm. Similarly, Nakamura [31], in a study of a fluorimetric method for the determination of saccharin in foods, describes saccharin as strongly fluorescent in the pH range from neutral to alkaline with excitation and emission maxima, respectively, at 277 nm and 410 nm.

In this study the aqueous solutions of saccharin were found to exhibit fluorescence with $\phi\approx0.04$ and a mono-exponential decay with a lifetime of $\tau=2.0$ ns.

Sodium saccharinate emission was examined in different solvents, like methanol, absolute ethanol, propanol, tert-butanol, DMF, DMSO, and cyclohexane/crown-ether. Control experiments showed that exposure of sodium saccharinate to light, under the fluorimetric assay conditions, does not lead to SO_2 photo-extrusion [32,33] and that saccharin is chemically stable at alkaline pH [34].

The excitation spectra of the saccharinate ion (data not shown) present a broad band in the region of the first absorption of the electronic spectra (Fig. 1). The absorption and emission spectra show a large Stokes shift and are not mirror image related. The emission spectra (with spectral distribution identical to the saccharin) follow Vavilov's law [35]. The sodium saccharinate quantum yield (determined against QBS) is about $\phi_F\approx0.015$ in polar aprotic solvents.

Sodium saccharinate emission is quenched by the iodide ion with a $k_q=3.1\times10^9\ M^{-1}\ s$.

The fluorescence lifetimes of saccharinate ion in various solvents are given in Table 1, and a typical decay profile is

Table 1
Fluorescence lifetimes of the saccharinate ion in different solvents

Solvent	τ (ns)	χ^2
Methanol-d4	2.01	1.300
Methanol	1.74	1.400
Ethanol	1.64	1.130
2-Propanol	1.62	1.040
Pentanol	1.65	1.040
Tert-butanol	1.74	1.076
DMF	1.93	1.000
Brij35 (10 mM)	1.96	1.114
Water	2.07	1.129
D_2O	2.50	1.131
CH_3CN	2.10	1.039
CTAC (10 mM)	2.17	1.162
Cyclohexane/18-crown-6-ether	2.26	1.400
DMSO	–	–

shown in Fig. 5. The decay times of sodium saccharinate in a series of homologous alcohols are in the range of 1.62 to 1.74 ns, increasing to a value close to $\tau = 2.0$ ns in DMF, acetonitrile, water, or water/surfactant and to $\tau = 2.26$ ns in cyclohexane/18-crown-6. Deuterium isotopic effects on the decay times [36] amount to 13% and 17% increases in D_2O and methanol-d_4, respectively.

Comparison of the electronic absorption, fluorescence decay and quantum yield of saccharin and sodium saccharinate leads to the conclusion that there is just one emissive species in aqueous solutions – the saccharinate ion. This fact is further corroborated by the saccharin pKa of 1.6 [37].

3.5. Sodium phthalimide fluorescence

No emission was detected for phthalimide solutions in water or organic solvents. Nevertheless, aqueous phthalimide solutions begin to emit at pHs above the phthalimide pKa [38]. However, the fluorophore is quickly consumed by alkaline hydrolysis ($k = 8.71\ M^{-1}\ s^{-1}$) [39] which yields a non-emissive product. These results suggest a phthalimide alkaline hydrolysis mechanism analogous to that proposed for succinimide [40], Scheme 3.

The phthalimide ring opening is slower in alcoholic media than in water. The absorption and emission bands are not mirror image related and show a large Stokes shift. The quantum yield does not change with the excitation wavelength. The emission maximum of the phthalimide ion in ethanol is around 450 nm (Fig. 5). The fluorescence quantum yields ($\phi_F \approx 0.04$) are similar in aqueous and ethanolic solutions. However, the lifetimes in water and ethanol are quite different, i.e., 4.1 and 0.87 ns respectively.

3.6. Fluorescence of sodium isatin

Isatin, like phthalimide and saccharin, is non-emissive. However, its photodecomposition gives products that present

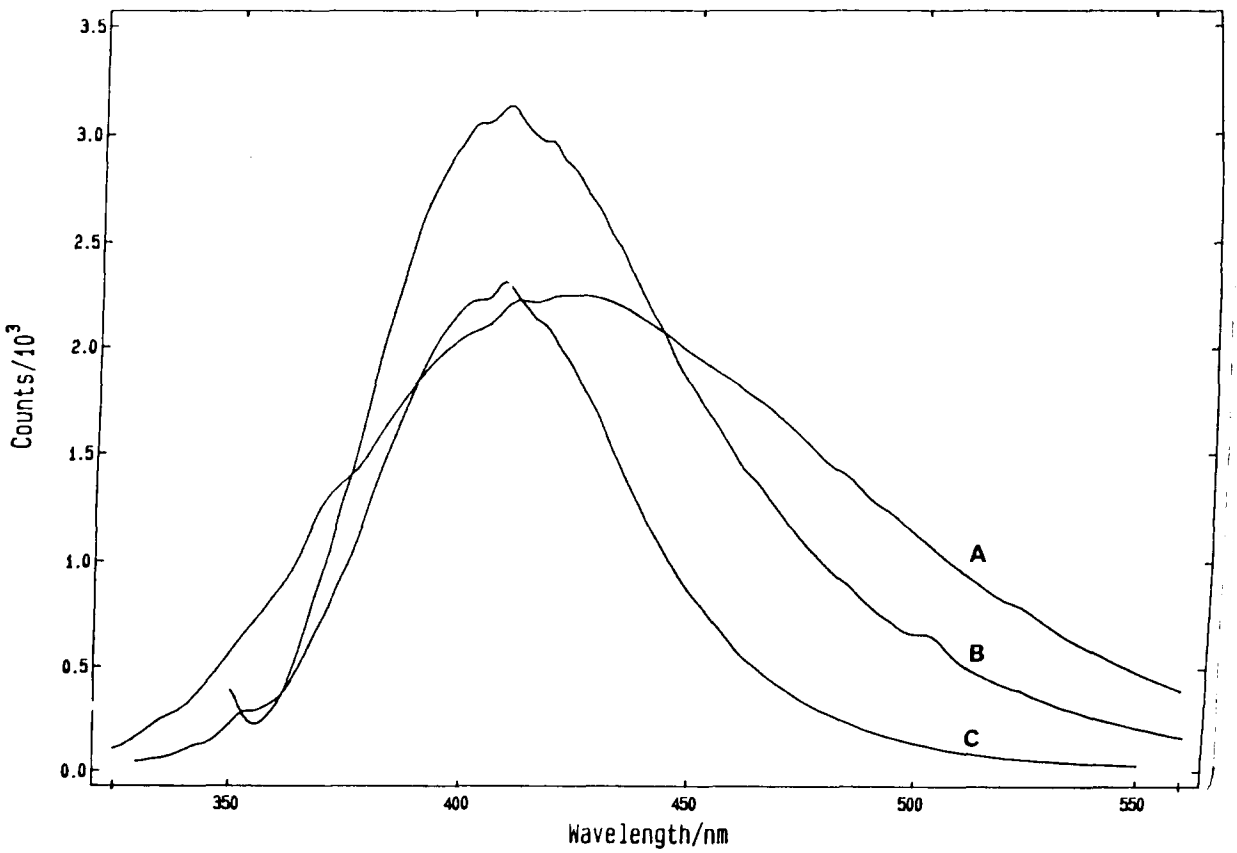
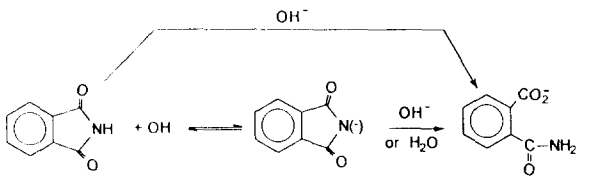


Fig. 4. Fluorescence spectra of sodium saccharinate in water (A), sodium phthalimide in ethanol (B), and sodium isatin in ethanol (C). All solutions were 5×10^{-5} M.



Scheme 3. Pathways of phthalimide hydrolysis to phthalamic acid.

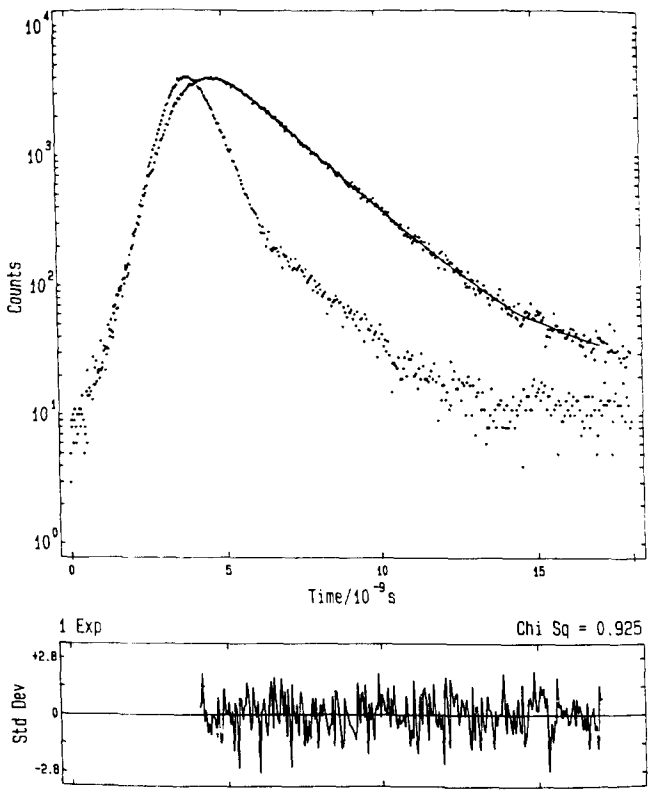


Fig. 5. Fluorescence decay of sodium saccharinate 5×10^{-5} M in water. $\lambda_{exc}=280$ nm and $\lambda_{em}=418$ nm.

a very weak emission ($\phi_F<10^{-4}$) in the range of 370–390 nm [23].

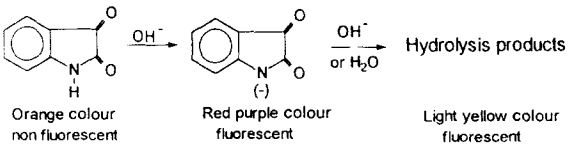
Sodium isatin does not emit when excited in its first electronic absorption band (λ maximum at about 500 nm, in ethanol). However, when excited in its second absorption band (an inflection around 300 nm) it fluoresces with a quantum yield of $\phi_F\approx0.002$, with an emission maximum at 420 nm (Fig. 4). The decay is mono-exponential with a lifetime of $\tau=5.7$ ns. Although fluorescence owing to an impurity or photodecomposition product(s) should not be ruled out *a priori*, no such impurity or product could be detected in any spectroscopic and chromatographic assay.

The isatin alkaline hydrolysis reaction sequence is presented in Scheme 4.

Sodium isatate in ethanol emits with a quantum efficiency of $\phi_F\approx0.07$ and shows a bi-exponential decay with $\tau_1=1.84$ and $\tau_2=5.62$ ns.

4. Discussion and conclusion

The results fall into two distinct types: (1) those for the aromatic heterocyclic systems bearing the imide (phthalimide) and o-sulfobenzimide (saccharin) functions, and (2) those for the oxamide (isatin) heterocyclic system, with anomalous fluorescence [41].



Scheme 4. Colour and emissive properties of isatin in alkaline solutions.

4.1. General considerations about the electronic absorption spectra

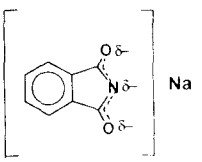
The characteristic absorption spectra of phthalimide is well known and has deserved theorical and experimental studies [42,43,44]. The phthalimide absorption bands in the near ultra-violet region are π, π^* in nature, perturbed by the substituents [45] of the benzene ring. The n, π^* transition localized on the imide functional group is the lowest energy band [43], which accounts for the observed lack of fluorescence.

The saccharin absorption spectra has been reported only for analytical purposes [46,47], with no band assignments. However, Kresze's investigation of benzothiaindanone-1,1-dioxide [48], a molecule related structurally to saccharin, provides clues to the spectral interpretation for saccharin. The sulfonyl group acts as an auxochrome, with no characteristic absorption bands in the near ultra-violet region. The π, π^* character of the transitions of the saccharin spectra allowed is clear. The intensity of the first absorption band at 276 nm ($\log\epsilon\approx2.8$) is comparable with the phthalimide n, π^* band [43].

4.2. Absorption of the conjugate bases

The structure and electronic configuration of the phthalimide ground state are well known [49]. Phthalimide is a planar molecule, with the electron pair of the imide nitrogen partly delocalized over the carbonyl groups, providing additional stabilization [50]. The conjugate base anion of phthalimide is still more stabilized (Scheme 5).

In solution, a resonance-stabilized ambident ion, like sodium phthalimide, should be present mostly as an ion pair with the alkali metal cation [10]. Usually, coordination of the alkali metal cation occurs at the higher electron density (harder) atoms [51] and the participation of contact or solvent-separated ion pairs depends on the solvent [54].



Scheme 5. Sodium phthalimide.

The functional moiety, [–CO–N–CO–]$^-$, of the phthalimide anion can be treated as a type of polymethine derivative [53], more properly an oxanol [54], substituted with nitrogen at the central atomic position [55]. The complete anion molecular structure, with the benzene ring connection, yields a polyene–polymethine coupling (with eleven atomic centers and twelve electrons) whose electronic energies and the consequent transition have been calculated successfully by the Hückel theory [56].

The Hückel calculus for the anion phthalimide indicates first an excited state with a neat increase of electron density on the aromatic ring and the carbons of the functional group; along with a zero coefficient on the nitrogen central atom and a decrease on the electron density of the oxygen atoms.

In the case of the saccharin molecule, the replacement of one of the carbonyl groups by a sulfonyl group provides a more stable ground state ambident anion [34], reflected in the saccharin pKa of 1.6 [37]. The significant stabilization of carbanionic centers adjacent to the sulfonyl groups has been realised by experimental and theoretical studies [57,58a,58b]. However, ultra-violet/visible absorption spectroscopic results point to strong conjugative effects in anions of β-ketosulfones in alkaline solutions [59,60].

Since the sulfonyl compounds have been treated as polymethine derivatives [61], the Hückel treatment of coupled polyene–polymethine can be again utilized. Thus a first excited state electronic configuration with a increase of electron density on the benzene ring is obtained.

4.3. Anions photophysics

The photochemistry of the sodium phthalimide has already been explored [62]. Irradiation of sodium phthalimide in methanolic solution in the presence of alkenes gives rise to adduct as the dominant product. Besides, arriving in the common photoproduct of neutral carbonyl compounds [63], its mechanism and excited state multiplicity were not further investigated. Sodium phthalimide is photostable under fluorimetric conditions and emits with a quantum yield fifty times higher than N-alkyl phthalimides [64]. The large observed Stoke's shift and the lack of a mirror image similarly reflect changes in electronic state geometry and significant solvation effects [65].

The complexity of the hydrogen-bond effects in protic solvents is indicated by the fluorescence lifetimes of sodium phthalimide in water and ethanol [66], i.e., 4.1 and 0.87 ns, respectively.

Sodium saccharinate exhibits a behaviour quite similar to that of sodium phthalimide. The large Stoke's shift and the absence of a mirror image relationship indicates the same factors cited for sodium phthalimide. Solvent effects are also noted in fluorescence quantum yields for protic and aprotic solvents.

The sodium saccharinate fluorescence lifetime exhibits the same deactivating effect in alcohols from methanol to pentanol. The hydrogen bond with sodium saccharinate with water seems to follow another hydrogen-bond mechanism or geometric pattern [66], giving a lifetime value of $\tau = 2.0$ ns. In lower dielectric media like cyclohexane/18-crown-6 the lifetime increases.

4.4. The oxamide (isatin) heterocyclic systems

Theoretical and experimental studies of the isatin electronic absorption spectrum are known [42,43]. The low-intensity broad absorption band in the visible region is assigned to a pure n, π^* transition involving the oxamide fragment, –NHCOCO–. The second electronic transition is well spaced (from the first band) and has a mixed n, π^* character [22,42,43]. Isatin photochemistry follows the course of the ordinary carbonyl compounds, yielding products of reduction and pinacol processes [23].

Although there are a number of descriptions of sodium isatin as an intermediate in isatin N-substitution [16,67–69], its photochemistry and photophysics are unexplored. The fluorescence of sodium isatin, excited in the second absorption band, is observed in all solvents tested; from water to HMPA. The Stoke's shift is smaller than that observed for sodium phthalimide and saccharinate. The 0–0 bands of the emission and S_2 absorption overlap and the spectra display an approximate mirror image relation.

The Hückel calculus about the S_1 and S_2 absorption state accounts for the anomalous fluorescence observed. The Hückel calculus describes an S_1 state with an increase of electron density on the atoms of the functional group, yielding a non-emissive excited state. In the S_2 state the calculus shows results similar to the sodium phthalimide and saccharinate studies, with an increase of electron density on the carbon atoms and a decrease on the heteroatoms. The internal charge–transfer S_2 character of the excited state shows the reported emission.

The observed hydrolysis of sodium isatin to form sodium isatate parallels that of sodium phthalimide to form phthalamic acid, suggesting a two-step mechanism involving formation of the isatin anion, followed by the hydrolysis reaction.

References

[1] L.M. Tolbert, in A. Padwa (ed.), *Organic Photochemistry*, Marcel Dekker, 1983, Vol. 6, p. 177.
[2] J. Plodinec and T.E. Hogen-Esch, *J. Am. Chem. Soc., 96* (1974) 5262.
[3] (a) M.A. Fox, in D.H. Volman, K. Gollnick and G. Hannond (eds.), *Advances in Photochemistry*, John Wiley and Sons, 1986, Vol. 13, p. 238.
(b) M.A. Fox and M. Chanon (eds.), Photoinduced electron transfer, part C: *Photoinduced electron transfer reactions: Organic substrates*, Elsevier, 1988.
[4] M.A. Fox, *Chem. Rev.*, (1979) 270.
[5] N.H. Velthorst, *Pure and Appl. Chem., 51* p. 85.
[6] L.M. Tolbert, S.M. Nesselroth, T.L. Netzel, N. Raya and M. Stapleton, *J. Phys. Chem., 96* (1992) 4492.
[7] J. March, *Advanced Organic Chemistry*, John Wiley and Sons, 1985, p. 154.

[8] J.P. Soumillion, *Top. Curr. Chem., 168* (1993) 93.
[9] D.F. Eaton, in D.H. Volman, K. Gollnick and G. Hammond (eds.), *Advances in Photochemistry*, John Wiley and Sons, 1986, Vol. 13, p. 448.
[10] M. Schlosser, *Angew. Chem. Internat. Ed., 3* (1964) 287.
[11] A. Vogel, *Textbook of Practical Organic Chemistry*, 4th edn., Longman, 1978, p. 649.
[12] T.W. Evans and W.M. Dehn, *J. Am. Chem. Soc., 52* (1930) 1028.
[13] E. Dykman, *Chem. Ind., 1* (1972) 40.
[14] L. Rice and G.R. Pettit, *J. Am. Chem. Soc., 76* (1954) 302.
[15] P.L. Salzberg and J.V. Supniewski, *Organic Synthesis Collect, I*, p. 119.
[16] A.E. Arbuzov and O.M. Shapskinkaya, *Trudy Kazam Klim, 16* (1951) 11.
[17] J.N. Demas and G.A. Crosby, *J. Phys. Chem., 75* p. 991.
[18] C.A. Parker, *Photoluminescence of Solutions*, Elsevier, 1968, p. 268.
[19] C.A. Parker and W.T. Rees, *Analyst, 85* (1960) 587.
[20] C.M. Lee and W.D. Kumler, *J. Org. Chem., 27* (1962) 2055.
[21] A. Arcoria and F. Bottino, *Ann. Chim., 51* (1961) 116.
[22] A. Mangini and R. Passerini, *Gazzeta Chimica Italiana, 85* (1955) 840.
[23] G. Haucke, B. Seidel and A. Graness, *J. Photochem., 37* (1987) 139.
[24] R.G. Ault, E. Hirst and R.A. Morton, *J. Chem. Soc.*, (1955) 1653.
[25] A.M. Ismail, *Alex. J. Pharm. Sci., 6*(1) (1992) 67.
[26] E. Sawicki, T.R. Hauser and T.W. Stanley, *Anal. Chem., 31* (1959) 2063.
[27] G. Stefanovic, L. Lorenc, R.I. Mamuzic and M.J. Mikailovic, *Tetrahedron, 6* (1959) 304.
[28] F.C. Almeida, V.G. Toscano, O. Santos, M.J. Politi, M.G. Neumann and P. Berci-Filho, *J. Photochem. Photobiol. A: Chem., 58* (1991) 289.
[29] P. Berci-Filho, V.G. Toscano and M.J. Politi, *J. Photochem. Photobiol. A: Chem., 43* (1988) 51.
[30] R. Brum, *Dermatologica, 152* (1976) 295.
[31] Y. Nakamura, *J. Ed. Hyg. Soc. Japan, 16* (1975) 368.
[32] N. Kamigata, T. Saegusa and S. Fujie, *Chem. Lett.*, (1979) 9.
[33] I.W.J. Still, in S. Patai, Z. Rapport and C.J.M. Stirling (eds.), *The Chemistry of Sulphones and Sulphoxides*, John Wiley and Sons, 1988, p. 873.
[34] O. De Garmo, G.W. Ashworth, C.M. Earker and R.H. Munch, *J. Am. Pharm. Assoc., 41* (1952) 17.
[35] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley, 1970, p. 142.
[36] Th. Forster and K. Rokos, *Chem. Phys. Lett., 1* (1967) 279.
[37] G.L. Fix and J.D. Pollack, *Anal. Chem., 52* (1980) 1591.
[38] J.A. Dean, *Lange's Handbook of Chemistry*, 13th edn., Mc GrawHill, 1985, Vol. 5, p. 54.
[39] P. Crooy and A. Brylants, *Bull. Soc. Chim. Belg., 73* (1964) 44.
[40] (a) J.T. Edwards and K.A. Terry, *J. Chem. Soc.*, (1957) 3527.
(b) O.H. Wheeler and O. Rosado, in Jacob Zabicky (ed.), The chemistry of functional groups, *The Chemistry of Amides*, Interscience, 1970, p. 335.
[41] N.J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, *Chem. Rev., 78*(2) (1978) 125.
[42] V. Galasso, *Gazzeta Chimica Italiana, 106* (1976) 571.
[43] V. Galasso and G.C. Pappalardo, *J. Chem. Soc. Perkin II*, (1976) 574.
[44] W. Fabian, *Theochem., 90* (1982) 249.
[45] L.F. Gladchenko, L.G. Pikulik and N.L. Belozarevich, *Opt. Spectrosk., 17* (1964) 209.
[46] M.M. Hussein, H. Jacin and F.B. Rodriguez, *J. Agric. Food Chem., 24*(1) (1976) 36.
[47] P.P. Losada, J.S. Lozano and G. Andara, *Anal. Bromatol. XLI-1*, (1989) 17.
[48] G. Kresze and W. Amann, *Spectrochim. Acta. 25A* (1969) 393.
[49] S.N. Bagchi and M.A. Kasen, *Indian Journ. Phys., 19* (1945) 93.
[50] J.D. Roberts and M.C. Casterio, *Basic Principles of Organic Chemistry*, W.A. Benjamin Inc., 1965, p. 553.
[51] O.A. Reutov, I.P. Beletskaya and A.L. Kurtis, *Ambident Anions*, Consultants Bureau, 1983, p. 5.
[52] C. Reichardt, *Solvents and Solvents Effects in Organic Chemistry*, VHC, 1990, p. 48.
[53] S. Dahne and F. Moldenhaver, in R.W. Taft (ed.), *Progress in Physical Organic Chemistry*, 1985, Vol. 15, p. 1.
[54] S.S. Malhotra and M.C. Whiting, *J. Chem. Soc.*, (1969) 3812.
[55] (a) E.B. Knott, *J. Chem. Soc.*, (1951) 1024.
(b) H. Kuhn, *Helv. Chim. Acta, 34* (1951) 2371.
[56] H.E. Zimmerman, *Quantum Mechanics for Organic Chemistry*, Academic Press, 1971, p. 1.
[57] S. Wolfe, A. Stolow and L.A. Lajohn, *Tetrah. Lett., 34* (1983) (38), 4071.
[58] (a) S. Wolfe, in F. Bernardi, I.G. Csizmadia and A. Mangini (eds.), *Organic Sulfure Chemistry*, Elsevier, 1985, p. 133.
(b) S. Oae and Y. Uchida, in S. Patai, Z. Rapport and C. Stirling (eds.), John Wiley and Sons, 1988, p. 583.
[59] H. Kwart and K. King, d-Orbitals in the chemistry of silicon, *Phosphorus and Sulfur*, Springer, 1977.
[60] E.A. Fehnel and M. Carmack, *J. Am. Chem. Soc., 71* (1949) 231.
[61] S. Dahne, *Zeitschrift Chem., 5* (1965) 448.
[62] R.S. Suarez and R.G. Segura, *Tetrah. Lett., 29*(3) (1988) 1071.
[63] P.H. Mazzochi, in A. Padwa (ed.), *Organic Photochemistry*, Marcel Dekker, 1981, Vol. 5, p. 421.
[64] V. Wintgens, P. Valat, J. Kossanyi, L. Biczok, A. Demeter and T. Berces, *J. Chem. Soc. Faraday Trans., 90*(3) (1964) 411.
[65] E.L. Wehry, *Modern Fluorescence Spectroscopy*, Plenum, 1976, Vol. 2, p. 279.
[66] S.N. Vinogradov and R.H. Linnell, *Hydrogen Bonding*, Van Nostrand Reinhold Co., 1971, p. 147.
[67] J. Harley-Mason and R.F.J. Ingleby, *J. Chem. Soc.*, (1958) 3639.
[68] G. Tacconi, P. Righetti, G. Desimoni, *J. Prakt. Chem., 315*(2) (1973) 339.
[69] G. Heller, *Ber.* (1907), band II, 1291.