Dyes and Pigments 85 (2010) 171–176

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Absorption and fluorescence of arylmethylidenoxindoles and isoindigo

Stanislav Luňák Jr.[a,*], Petra Horáková[a], Antonín Lyčka[b,c]

[a] Department of Organic Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 95, Pardubice CZ-532 10, Czech Republic
[b] Research Institute for Organic Syntheses, Rybitví 296, Rybitví CZ-533 54, Czech Republic
[c] University of Hradec Králové, Faculty of Education, Rokitanského 62, CZ 500 03 Hradec Králové 3, Czech Republic

ARTICLE INFO

Article history:
Received 20 August 2009
Received in revised form
29 October 2009
Accepted 1 November 2009
Available online 12 November 2009

Keywords:
Absorption
Fluorescence
Density functional theory
Isoindigo
Arylmethylidenoxindole

ABSTRACT

A series of arylmethylidenoxindoles was synthesized by acid or base catalysed condensation of substituted aldehydes with oxindole. The products were formed as mixtures of *Z*- and *E*-isomers that were separated using column chromatography and identified by ^{1}H and ^{13}C NMR. The effect of substituents on absorption maxima was investigated both experimentally and theoretically, based on time dependent density functional theory. Low temperature absorption spectroscopy in a solvent glass enabled identification of the position of the 0-0 vibronic bands. The spectral features of the parent *Z*-benzylidenoxindole were compared to those of *trans*-isoindigo and *trans*-stilbene. Fluorescence of arylmethylidenoxindoles in solution was not observed, as *E*–*Z* isomerization represents a dominant deactivation channel after irradiation; when this geometrical isomerization was sterically hindered at low temperature solvent glass or in solid, fluorescence of planar *Z*-isomers was observed.

1. Introduction

Z-Benzylidenoxindole (**I**) is a π-isoelectronic N-analogue of isoaurone, a parent chromophore of naturally occurring yellow pigments [1]. The compound **I** was prepared in both *Z*- and *E*-isomeric forms [2] and the X-ray structural data are available for them [3,4] (file LOHZAJ in Cambridge structural database (CSD) for *Z*-isomer). The compound **I** can be also formally considered as a hemistilbene/hemiisoindigo hybrid (Fig. 1).

There were several reasons for our interest on this class of compounds. We are generally interested in the dyes arising from a relatively simple condensation of aldehydes with heterocycles containing an activated methylene group [5]. N-acylated **I** was reported to show solid state fluorescence [4], which is also of our interest, because of its potential use in OLED devices [6]. While the spectral properties and excited state processes occurring in *trans*-stilbene were widely studied, there is a limited knowledge of the effect of its cyclization into one (**I**) or two (isoindigo) pyrrolinone rings on the absorption spectra and excited state behaviour. A recent theoretical study of the indigo isomers has found a significant discrepancy between theoretical excitation energy and a position of long wavelength absorption maximum of *trans*-isoindigo [7]. An explanation based on underestimation of excitation energies of charge-transfer transitions by time dependent density functional theory (TD DFT) is not supported by our experience with related molecular structures [8], so we decided to reinvestigate this feature.

The aim of this paper is to study in detail the relation between structure and absorption spectra of arylmethylidenoxindoles and isoindigo and to look for their so far unknown fluorescence properties in various environments, i.e. in room temperature dimethyl sulfoxide (DMSO) and 2-methyltetrahydrofuran (MTHF) solutions, low temperature MTHF glass and polycrystalline solid state. We have synthesized a set of model compounds shown in Fig. 1. The biphenylyl compound (**II**) was synthesized for the first time in order to investigate an effect of a conjugated chain elongation on the spectral properties. The derivative with strong electron-donating group in *para* position of pendant phenyl (**III**) is known in both its isomeric forms [3]. There are several studies on the antitumour activity of **III**, that we will not review here. The compound **III** also appeared as an example of a dye for mass colouration of plastics [9], but it is not clear whether the *Z*- or *E*-isomer or their mixture was used.

Structural calculations of arylideneoxindoles were reported [4]. No quantum-chemical study of spectral properties of these chromophores was found. That is why DFT was used to geometry calculations and TD DFT to calculate the vertical excitation energies, with the same hybrid B3LYP exchange – correlation functional. The solvent effect was involved through polarized continuum model (PCM). No experimental absorption spectra of the compounds under study have been reported other than in solution and fluorescence has not been investigated up until now.

---

* Corresponding author. Tel.: +420 602437863; fax: +420 466635292.
E-mail address: stanislav.lunak@seznam.cz (S. Luňák Jr.).

doi:10.1016/j.dyepig.2009.11.001

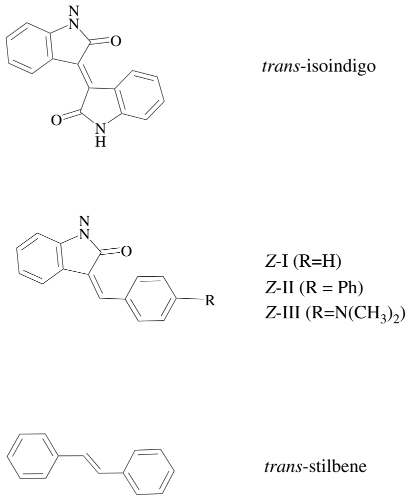

Fig. 1. Chemical structure of synthesized compounds (drawn as of *Z*-isomers) together with *trans*-isoindigo and *trans*-stilbene formulas.

2. Results and discussion

2.1. Syntheses

trans-Isoindigo was synthesized by a condensation of oxindole and isatin [10]. Compounds **I** and **II** were synthesized by *p*-toluenesulfonic acid catalysed condensation of benzaldehyde (4-biphenylcarboxaldehyde) with oxindole. Compound **III** was synthesized by base (piperidine) catalysed condensation of p-dimethylaminobenzaldehyde and oxindole. The reaction mixture always contained both the *E*- and *Z*-isomers. Compounds **I** and **III** crystallized as *E*-isomers and were converted to *Z*-isomers by an exposure of their solutions to daylight. Pure *Z*-**II** crystallized from a hot reaction mixture, while *E*-**II** was obtained from cooled filtrates. Final products were obtained by flash column chromatography on silica (acetone – hexane 2:3). The identity of both isomers of **I** and **III** was checked by a comparison of their melting points with the published data [3] and the purity was monitored by elemental analysis and mass spectrometry.

The syntheses of both isomers of a new compound **II** are described in detail in Experimental. The isomers were preliminary assigned according to the shifts of their absorption spectral maxima after irradiation (*Z* → *E* hypsochromic and hypochromic, *E* → *Z* bathochromic and hyperchromic) and checked by recently verified methodology based on $J(^{13}C, ^1H)$ coupling constants [5]. We utilised a method proposed by Cho et al. [11], based on a stereochemical dependence of $^3J(^{13}C, ^1H)$ coupling constants on a C=C double bond. Cho et al. found that coupling constant of carbon *trans* to the olefinic proton is considerably larger to that of carbon *cis* to the same proton utilising single crystal X-ray data in the solid state and heteronuclear Overhauser effect in solution in suitable model compounds. Stereochemical dependence of the $^3J(^{13}C, ^1H)$ coupling constants were studied in the fragment HN–**C**(=O)–C(=C**H**–)– having measured proton-coupled ^{13}C NMR spectra of chromatographically separated isomers of compound **II** at digital resolution better than 0.5 Hz/point. The NH–**C**=O resonances gave a dd in the proton-coupled ^{13}C NMR spectra. The small coupling constant in the dd in both cases corresponds to the interaction of carbonyl carbon with NH proton ($^2J(^{13}C(O)N^1H)$ = 2.5 Hz). The coupling constant $^3J(^{13}C(O)C{=}C^1H)$ = 12.1 Hz belongs to *Z* form on double bond (compound *Z*-**II**) while $^3J(^{13}C(O)C{=}C^1H)$ = 6.9 Hz belongs to *E* form on double bond (compound *E*-**II**).

2.2. DFT ground state geometry and energy

Restricted B3LYP/6-311++G(d,p) DFT calculations in vacuum resulted in a strictly planar geometry for *Z*-isomers of all three arylmethylidenoxindoles (except for the phenyl–phenyl torsion in *Z*-**II**) and *trans*-stilbene. On the other hand, all three *E*-isomers were computed to be non-planar with pendant phenyl ring rotated out of oxindole plane. The experimental [3] dihedral angles for both *Z*-**I** (8.0°) and *E*-**I** (49.7°) are rather higher than the theoretical ones (0°, resp. 37.0°), that can be ascribed to packing effects in the crystal, not being taken into account in these calculations. The corresponding dihedral angles of *E*-**II** and *E*-**III** were computed to be 35.2° and 28.6°, respectively. The dihedral angle between both phenyls rings was 38.1° for *Z*-**II** and 38.9° for *E*-**II**.

Z-isomers are generally only a bit more stable than *E*-isomers by calculation. The energy differences are 0.32 kcal mol^{-1} (**I**), 0.60 kcal mol^{-1} (**II**) and 1.35 kcal mol^{-1} (**III**). The thermodynamic stability of both isomers is thus very similar, that can be one of the reasons of their simultaneous rise in a reaction mixture.

The central ethylenic bond is significantly elongated when going from *trans*-stilbene (theor. 1.346 Å, exp. [12] 1.326 Å) to *trans*-isoindigo (theor. 1.377 Å, exp. [13] 1.369 Å), which agrees with a significant decrease of the frequency of the corresponding C=C stretching mode [10]. Thus *Z*-**I** is their true hybrid, as the corresponding bond length lies between those ones of its two symmetrical parent compounds both theoretically (1.359 Å) and experimentally [3] (1.350 Å).

There is a known discrepancy between the calculated non-planarity [7,10] and experimental planarity [13] of *trans*-isoindigo. So we have focused on this problem in a more detailed manner. The dependence of the total energy of *trans*-isoindigo on the central double bond torsion, as computed in vacuum and DMSO solution involved by PCM, is shown in Fig. 2. The energy minimum shifts from 10.0° in vacuum to 14.6° in DMSO, as the polar environment more efficiently stabilizes the non-planar and thus polar structure through solute–solvent interaction. The minimum is shallow and the energy of a transition state (180°) and the structure with a dihedral angle 150° is almost the same in DMSO.

2.3. Absorption and fluorescence of arylmethylidenoxindoles

All three arylmethylidenoxindoles easily undergo a photochemical *Z*–*E* isomerization in both directions in solution. The absorption spectra of non-planar *E*-isomers show hypsochromic and hypochromic shift relative to the *Z*-isomers (Table 1) caused by an imperfect conjugation.

No fluorescence of any arylmethylidenoxindole was observed in DMSO or MTHF solution at room temperature. On the other hand, all three *Z*-isomers of **I**, **II** and **III** show fluorescence both in rigid

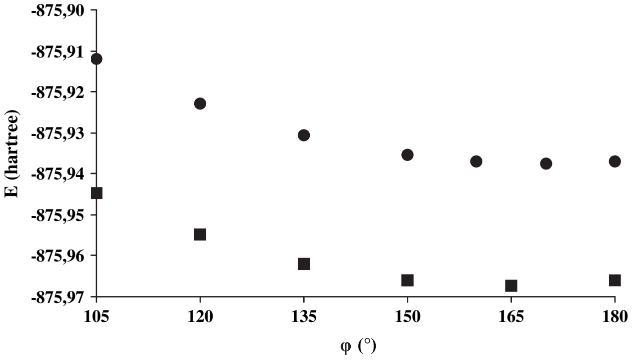

Fig. 2. The dependence of a total energy of *trans*-isoindigo on a central dihedral angle in vacuum (●) and DMSO (■).