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Heteroatom effect on the radiative and reactive photobehaviour of *E*,*E*-1,2-distyrylbenzene

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Abstract

The heteroatom effect on the radiative and reactive relaxations of *E*,*E*-1,2-distyrylbenzene (DSB) has been studied by stationary and time-resolved techniques on three compounds where the side phenyl (Ph) groups were replaced by 4′-pyridyl (4P), 2′-thienyl (2T) and 2′-furyl (2F) groups. Contrary to the case of the hydrocarbon, whose photoisomerization is accompanied by substantial degradation, the *E*,*E* → *Z*,*E* photoisomerization prevails in the hetero-analogues, particularly in the thienyl derivative. The lack of conjugation in these 1,2-substituted benzenes leads to a decrease in the fluorescence yield with respect to their 1,4 and 1,3 analogues (particularly in the presence of the heteroatoms), which is accompanied by an increase of the photoreaction quantum yield for the pyridyl- (significant) and thienyl- (very small) derivatives, whilst internal conversion is the prevalent deactivation pathway of the furyl derivative.

Keywords: Di-(heteroarylethenyl)benzenes; Photoisomerization; Fluorescence

1. Introduction

The photochemistry of stilbene-like compounds has been thoroughly investigated in the last decades because of their interest from the point of view of both mechanistic photochemistry and potential use in applied research. The photobehaviour of compounds containing repeating phenylenevinylene units has received wide attention since delocalization of π electrons in their electronically excited states can induce new properties which can have implications in the field of material science and particularly in optoelectronics [1].

Distyrylbenzene (DSB) can be considered as a model compound for such systems [2]. The photoisomerization of the *para*-substituted 1,4-DSB (linear conjugation) [3,4] and of the *meta*-substituted 1,3-DSB (crossed conjugation) [5–7] has been particularly investigated. The effect of nitrogen and sulphur heteroatoms in the side and central rings has been the object of an extensive study in our laboratory [4,5,7,8]. More scattered data on the photobehaviour of the sterically crowded *ortho*-substituted 1,2-DSB have been reported [2,5,9].

The present paper describes the results of an investigation on the heteroatom effect on the radiative and reactive relaxations of *E*,*E*-1,2-DSB. In the compounds investigated (Scheme 1), the side phenyl groups are replaced by pyridyl, thienyl and furyl groups. Previous investigation on the behaviour of the hydrocarbon under prolonged irradiation has shown that the *E*,*E* → *Z*,*E* photoisomerization is accompanied by large formation of cyclization and degradation products [9]. Our results, obtained in mild conditions, whilst confirming the substantial formation of side photoproducts for the hydrocarbon, showed that geometrical isomerization is the prevalent reactive relaxation of the hetero-analogues, particularly for the thienyl compound.

The lack of conjugation in these 1,2-substituted benzenes leads to a decrease in the fluorescence yield with respect to their 1,4 and 1,3 analogues (particularly in the presence of the heteroatoms), which is accompanied by an increase of reactivity for the pyridyl- (significant) and thienyl- (very small)

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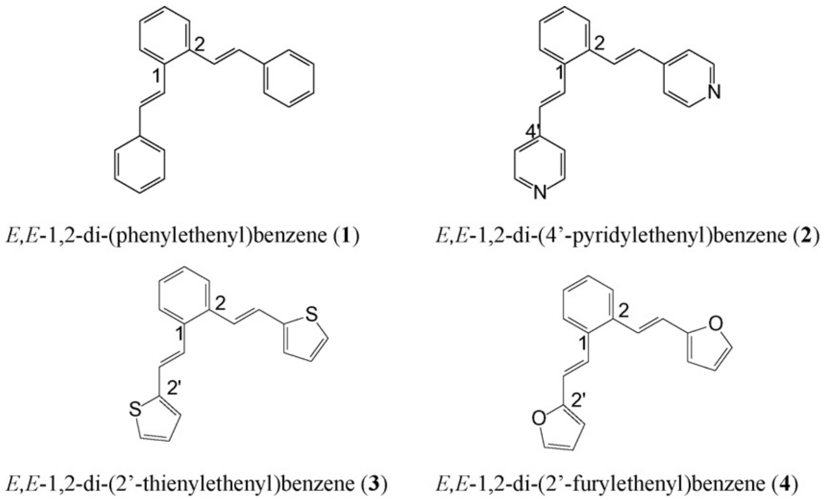


E,*E*-1,2-di-(phenylethenyl)benzene (**1**)
E,*E*-1,2-di-(4’-pyridylethenyl)benzene (**2**)
E,*E*-1,2-di-(2’-thienylethenyl)benzene (**3**)
E,*E*-1,2-di-(2’-furylethenyl)benzene (**4**)

Scheme 1.

derivatives, whilst the furyl derivative mainly relaxes by internal conversion.

Although the present study was mainly addressed to the photobehaviour of the *E*,*E* stereoisomers, some preliminary results on the back *Z*,*E* → *E*,*E* photoisomerization are also reported.

2. Experimental

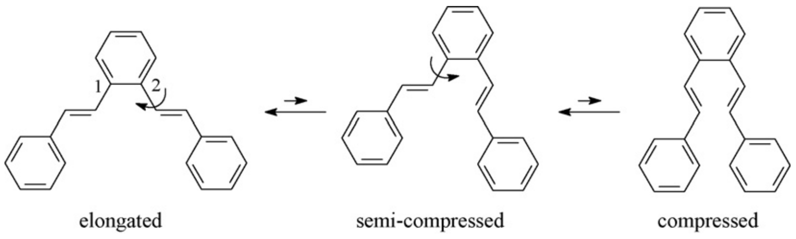
The compounds investigated are shown in Scheme 1. The phenyl- (Ph) and 4′-pyridyl- (4P) derivatives (prepared for previous works [5] and the 2′-thienyl (2T) derivatives were synthesized by one of us (G.G.) at the Padua laboratory by application of a two-fold Wittig reaction to difunctional reactants, benzyltriphenyl-phosphonium chloride (appropriately changing the reagents, for the hetero-derivatives) and 1,2-dicarboxyaldehyde. The 2′-furyl- (2F) derivative was synthesized by one of us [10] also by Wittig reaction but starting from *o*-xylen-diphosphonium salt and two equivalents of 2-furancarboxaldehyde. The isomers were separated and carefully purified by preparative HPLC and then characterized by ^{1}H NMR spectrometry (see Appendix A, supplementary data for compound **3**, Ref. [5] for **1** and **2** and Ref. [10] for **4**).

The solvents were 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP), benzene and acetonitrile from Fluka, spectrophotometric grade.

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence spectra were measured by a Spex Fluorolog-2 F112AI spectrofluorimeter. Dilute solutions (absorbance <0.1 at the excitation wavelength, λ_{exc}) were used for fluorimetric measurements. The emission and photoreaction quantum yields were determined at λ_{exc} corresponding to the maximum of the first absorption band ($\lambda_{\max}$), except when otherwise indicated. 9,10-Diphenylanthracene in cyclohexane was used as fluorimetric standard ($\phi_F = 0.90$ in de-aerated solvent [11]).

For photochemical measurements (potassium ferrioxalate in water as actinometer), a 150 W high pressure xenon lamp coupled with a monochromator was used. The photoreaction (solute concentrations $\sim 10^{-4}$ M) was monitored by HPLC using a Waters apparatus equipped with analytical Simmetry or Jupiter C18 (4.6 mm × 250 mm; 5 μm) and Prontosil 200-3-C30 (4.6 mm × 250 mm; 3 μm) columns and UV detector. Water/acetonitrile mixtures were used as eluents. The monitoring wavelength was at the isosbestic point; otherwise corrections for different absorption coefficients were introduced. The disappearance quantum yield (ϕ_{dis}) was measured using thioxant-9-one in acetonitrile as internal standard. The conversion percentage was held at below 8% to avoid the competition from the back photoreaction. Sensitized experiments were carried out using biacetyl in benzene or 2,3-dithienylketone in cyclohexane as triplet donors.

Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method. The triplet state was investigated by nanosecond laser flash photolysis ($\lambda_{\mathrm{exc}} = 355$ nm) using a Continuum Surelite II Nd:YAG laser.



Scheme 2. Conformational equilibria of *E*,*E*-1,2-distyrylbenzene.