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Photophysics, photochemistry and thermal stability of diarylethene-containing benzothiazolium species



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ABSTRACT

The photophysics, photochemistry and thermal stability of four 1-aryl-2-(*N*-methyl-2-benzothiazolium) ethene iodides (aryl: phenyl, 1-naphthyl, 9-phenanthryl and 9-anthryl) were studied. Although the absorption spectra are found to be hypsochromic-shifted, fluorescence spectra are bathochromic-shifted. The dipole moment in the relaxed excited state was found to be larger than that in the ground state. To investigate effects of *N*-methylation and the aryl-ring size, a detailed comparison was made between those in the present work (of charged compounds) and previous studies of their neutral analogues, with computed electron affinity and ionisation potentials serving to rationalise the experimentally observed bathochromic shifts in absorption and emission spectra. The kinetics of thermal isomerisation depend strongly on the nature of the aryl moiety and solvent; the larger the aryl ring, the slower the rate of isomerisation. The fastest isomerisation process was found to take place in MeOH. The anthryl derivative did not isomerize either by light- or heat-exposure, due to high energy barriers of rotation around the ethenic bond. Based on the significant blue-shift of the *Z*-isomer absorption maximum relative to that of the *E*-isomer, and the high percentage of *Z*-isomers in the photostationary state, these compounds may serve as potential promising candidates for optical data-storage applications.

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1. Introduction

Photo-induced *Z*–*E* isomerisation about double bonds has long been a subject of intense research, motivated by either pure-chemistry or more applied, industrial, perspectives. For instance, photoisomerisation about a carbon–carbon double bond in the rhodopsin chromophore is the initial trigger for light recognition in human eyes [1]. The photoisomerisation of urocanic acid acts as a ‘natural sunscreen’, protecting DNA from photo-damage [2]. Owing to photoisomerisation, diarylethenes are a popular example of photo-isomerizable molecules; they have found widespread application as sensitizers and other additives in the photographic industry [3–7], ion recognition [8], as optical-recording media in laser disks [9], as flexible dyes [10], laser dyes [11], and, indeed, as

optical sensitizers in various other fields [12–15]. It has been reported that this class of dyes act as imaging agents for Alzheimer disease [16], as effective biological markers [17], and as promising candidate dye sensitizers in solar cells [18]. Azastilbenes and their quaternary salt, stilbazolium, constitute good representative examples of the diarylethene family (cf. Fig. 1). Motivated by the desire to make further progress into potential modern technological applications, the synthesis of new photo-isomerisable molecules and characterisation of their photophysics, photochemistry and thermal stability in different environments are *sine qua non*.

The *Z* ↔ *E* photoisomerisation of neutral azastilbene derivatives has been the subject of several studies [19–21]. The introduction of a positive charge (upon quaternisation) into them gives rise to a new phenomenon, driven and controlled by heat, namely thermal *Z* → *E* isomerisation [20,22–29]; this is the ‘dark’ counterpart of the *E* → *Z* photoisomerisation reaction (cf. Fig. 1). Quaternary salts of 1-alkyl-4-(–4′-*R*-styryl) quinolinium iodide (e.g., *R* = NO₂, H or CH₃) exhibit thermal *Z* → *E* isomerisation at room temperature [24–26], whilst neutral analogues do not [19]. For stilbazolium salts, the rate

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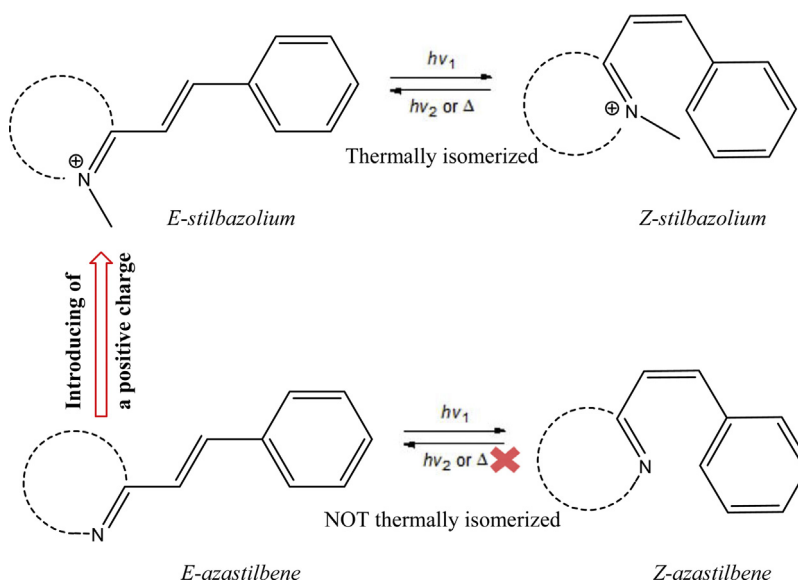


Fig. 1. Introduction of positive charge to azastilbene adapts it to convert thermally by heat.

constant has been found to depend significantly on the polarity of the solvent and to a smaller extent on the substituent in the 4-position of the styrene ring, as well as on the nature of the anion [26].

About two decades ago, we studied, in various solvents, the *N*-methylation of 1-(2-naphthyl)-2-(2-benzothiazolyl) ethene and the kinetics of thermal *Z* → *E* isomerisation. Recently, we observed *N*-methylation of 1-(9-phenanthryl)-2-(2-benzothiazolyl) ethene (9-PhBE) [21,22], where the *N*-methylated form (9-PhBEI, Fig. 2) back-isomerises thermally [26], whilst, intriguingly, the neutral analogue does not [22]. We also established the effect of *N*-methylation on the photophysics on 1-(9-anthryl)-2-(2-benzothiazolyl) ethene (9-ABE) and its quaternary salt (9-ABEI, Fig. 2) [30]; dual emission was observed for both compounds, which was found to originate from the involvement of locally-excited (LE) states and either twisted intramolecular charge transfer (TICT) or intramolecular exciplex formation in the excited state, respectively. Previously [22], we studied the effect of aryl ring size on the photophysics and photochemistry of styrylbenzothiazole (PBE) via systematic replacement of the phenyl ring of 1-phenyl-2-(2-benzothiazolyl) ethene with naphthyl (1-NBE) and phenanthryl (9-PhBE) rings. Increasing the size of aromatic rings served to increase

the extent of ICT between the benzothiazolyl and aryl fragments. This was confirmed by red shifts of their various spectra, along with increases in their dipole moment and Stokes shift. The percentage of the *Z*-isomers due to photoisomerisation was found to be size-dependent for the given solvent and irradiation wavelength; this was found to be in the order PBE > 9-PhBE > 1-NBE [22]. In interesting work by other investigators, the solvent and substituent effects on the photophysics of styryl-ethylbenzothiazolium derivatives, possessing different electron-withdrawing or electron-donating groups, have also been studied [31,32]. The formation of aggregated structures was also observed at higher concentrations of the benzothiazolium bromides [31].

Bearing in mind this photochemical activity and previous studies of similar molecular systems as discussed above, we seek to study in the present work the photophysics and photo-/thermochemical aspects of back *E* ↔ *Z* isomerisation, motivated by the tantalising possibility of realising temperature-controlled photochromic end-applications. In particular, important goals are the investigation of the effect of replacing the phenyl ring by larger polycyclic aromatic rings, as well as the nature of solvent on spectral characteristics and rate of photo- and thermal-isomerisation. We also use Density Functional Theory (DFT) to study the

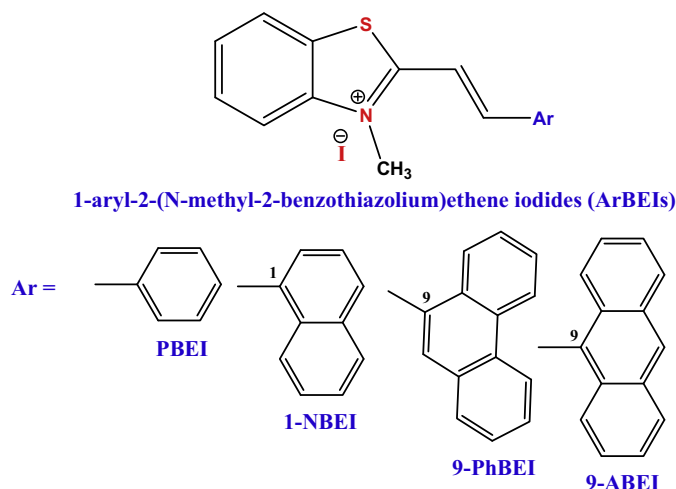


Fig. 2. The molecular structure of 1-aryl-2-(*N*-methyl-2-benzothiazolium) ethene iodides (ArBEIs) with their abbreviated names.

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