

## A push–pull 4a,4b-dihydrophenanthrene†

Frederick D. Lewis,\*<sup>a</sup> Todd L. Kurth<sup>a</sup> and Rajdeep S. Kalgutkar<sup>ab</sup>

<sup>a</sup> Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208 USA.

E-mail: lewis@chem.northwestern.edu

<sup>b</sup> Science Research Center, 3M Company, St. Paul, MN 55144, USA

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**Irradiation of (Z)-3-cyano-3'-aminostilbene in the absence of oxygen yields a push–pull substituted dihydrophenanthrene with substantial quinoidal character as evidenced by the pronounced solvent dependence of its absorption spectrum.**

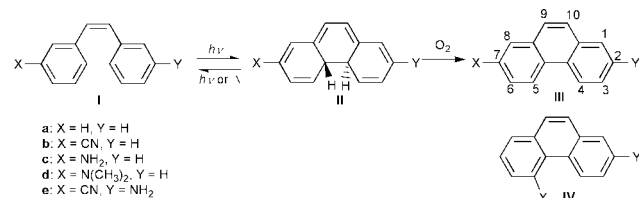
The photocyclization of diarylethenes is among the most extensively studied of photochromic reactions.<sup>1–5</sup> The prototype for this reaction is the photocyclization of the colorless (Z)-stilbene **Ia** to the yellow 4a,4b-dihydrophenanthrene **IIa**, which is rapidly converted to phenanthrene in the presence of oxygen (Scheme 1). In the absence of oxygen **IIa** undergoes ring opening to reform **Ia** both thermally and photochemically. Lack of thermal stability and sensitivity to oxygen has limited the utility of stilbene photocyclization in photochromic applications. The search for photochromic molecules which are thermally stable even in the presence of oxygen has led to the development of diarylethenes with heterocyclic aryl groups.<sup>5,6</sup> The presence of an electron donating group on one heterocycle and an electron accepting group on the other has provided photochromic systems that absorb throughout the visible and into the infrared. Curiously, the photochemical generation of push–pull stabilized 4a,4b-dihydrophenanthrenes has not been investigated.

The effects of single electron donating or accepting substituents on the quantum yield for phenanthrene formation ( $\Phi_p$ ) from (Z)-stilbenes in the presence of oxygen was investigated by Güsten and co-workers.<sup>7,8</sup> They report higher values of  $\Phi_p$  for 3-cyanostilbene **Ib** and 3-aminostilbene **Ic** (0.012 and 0.28, respectively) than for their 4-substituted isomers. Irradiation of either **Ib** or **Ic** in the presence of oxidizing agents results in the formation of both 2- and 4-substituted phenanthrenes (**III** and **IV**), in a ca. 3.5:1 ratio. Muszkat *et al.*<sup>9</sup> have investigated the anaerobic irradiation of several monosubstituted (Z)-stilbenes and report a higher quantum yield for formation of dihydrophenanthrene **IIb** from **Ib** (0.012) than for its 4-substituted isomer. The photochemistry of a large number of push–pull 4,4'-disubstituted stilbenes including 4-cyano-4'-aminostilbene has also been investigated.<sup>10–13</sup> These stilbenes undergo reversible *trans*–*cis* photoisomerization. However, to our knowledge there have been no reports of their photocyclization. As part of our study of the photochemical behavior of aminostilbenes,<sup>14–17</sup> we have investigated the anaerobic irradiation of **Ic**, its *N,N*-dimethylamino analog **Id**, and (Z)-3-amino-3'-cyanostilbene **Ie**.

Irradiation of the (Z)-3-aminostilbenes **Ic**, **Id**, and **Ie** in freeze–pump–thaw degassed cyclohexane (C<sub>6</sub>H<sub>12</sub>) or acetonitrile (CH<sub>3</sub>CN) solution promptly followed by acquisition of the absorption spectrum results in the observation of a broad absorption band at long wavelengths.<sup>18</sup> The deconvoluted absorption spectra of **IIc**, **IIId**, and **IIe** in acetonitrile solution are shown in Fig. 1. These spectra are obtained by means of singular value decomposition (SVD)-self modeling from a matrix of absorption spectra obtained at different conversions (see: supplementary information). This procedure also establishes the presence of one major dihydrophenanthrene product along with the (Z)- and (E)-stilbenes in each case. The major products are assigned structures **IIc**–**IIe** on the basis of formation of the corresponding 2-aminophenanthrenes **IIIc**–**IIIe** as the major products obtained from the irradiation of aerated solutions. In the case of **Ie** irradiation of an aerated solution results in the formation of **IIIc** and **IIIe** in a 4.3:1 ratio, but no detectable 4-amino-7-cyano isomer.<sup>19</sup> The absence of evidence for the presence of 4-aminodihydrophenanthrene products under anaerobic conditions may reflect more rapid thermal ring opening of the 4-amino-substituted dihydrophenanthrenes.

The absorption band of **IIc** (Fig. 1) is rapidly bleached by visible light but is stable in the dark for a period of several days in CH<sub>3</sub>CN solution and undergoes repeated formation and bleaching without degradation. This permits acquisition of the <sup>1</sup>H NMR spectrum of **IIc** as a mixture with **Ic**.<sup>20</sup> Salient features of the spectrum include singlets at 3.23 and 3.27 ppm assigned to the 4a,4b protons and unresolved multiplets between 5–7 ppm assigned to the vinyl protons.<sup>3</sup> Optimum conversions of **Ic** to **IIc** are obtained using monochromatic 276 nm irradiation as observed for conversion of **Ia** to **IIa** by Muszkat and Fischer.<sup>21</sup> The absorption bands of **IIId** and **IIe** bleach rapidly in the dark and thus no attempt was made to obtain their NMR spectra.

Absorption spectral data for the (Z)-stilbenes **Ia**–**Ic**, and **Ie** in C<sub>6</sub>H<sub>12</sub> and CH<sub>3</sub>CN are summarized in Table 1. The presence of 3-amino substituents in **Ic** and **Ie** results in a large red-shift in their absorption bands compared to that of **Ia**. Similar red-shifts are observed for the *trans* isomers of **Ic** and **Id** and are attributed



Scheme 1

† Electronic supplementary information (ESI) available: electronic absorption spectral matrices for the irradiated aminostilbenes and SVD analyses (6 figures). See <http://www.rsc.org/suppdata/cc/b1/b104510p/>

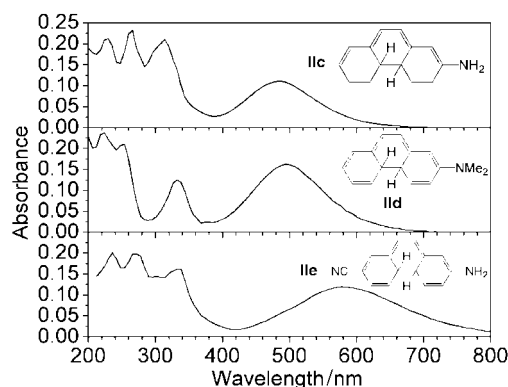


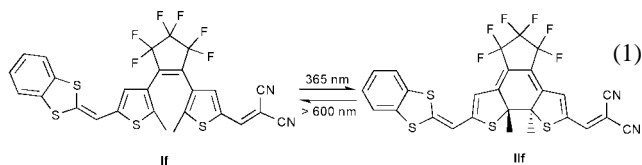
Fig. 1 Deconvoluted absorption spectra of the aminodihydrophenanthrenes **IIc**, **IIId**, and **IIe** in acetonitrile solution.

**Table 1** Absorption spectral data and calculated dipole moments for (*Z*)-stilbenes and dihydrophenanthrenes

| Compd.                 | $\lambda_{\text{max}}/\text{nm}$<br>(C <sub>6</sub> H <sub>12</sub> ) | $\lambda_{\text{max}}/\text{nm}$<br>(CH <sub>3</sub> CN) | $\mu_{\text{g}}/\text{D}^a$ | $\mu_{\text{e}}^{\text{FC}}/\text{D}^b$ |
|------------------------|---|--|-----------------------------|---|
| <b>Ia</b>              | 276   | 276  |                             |   |
| <b>Ib<sup>c</sup></b>  | 277   |  |                             |   |
| <b>Ic<sup>d</sup></b>  | 315   | 320  |                             |   |
| <b>Ie</b>              | 317   | 328  |                             |   |
| <b>IIa<sup>e</sup></b> | 450   | 450  | 0.7                         | 0.7                                     |
| <b>IIb<sup>e</sup></b> | 467   |  |                             |   |
| <b>IIc<sup>d</sup></b> | 470   | 482  | 2.4                         | 11.4                                    |
| <b>IId</b>             | 482   | 494  | 2.1                         | 11.7                                    |
| <b>IIe</b>             | 530   | 578  | 7.2                         | 16.0                                    |

<sup>a</sup> Calculated ground state dipole moment. <sup>b</sup> Dipole moment of the Franck–Condon singlet state calculated using eqn. (2). <sup>c</sup> Data from ref. 8. <sup>d</sup> Data from ref. 17. <sup>e</sup> Data from ref. 3.

to splitting of the long-wavelength band which results from configuration interaction.<sup>15,16</sup> Much smaller shifts are observed for the 3-cyano substituents in **Ib** (vs. **Ia**) and **Ie** (vs. **Ic**).<sup>9</sup> Also reported in Table 1 are the absorption maxima for the dihydrophenanthrenes **IIa–IIe**. The substituent-induced red-shifts are larger than those observed for the corresponding (*Z*)-stilbenes and similar shifts are observed for the 3-amino and 3-cyano substituents in **IIb** and **IIc**. The shift for **IId** is larger than that for **IIc**, as previously observed for (*E*)-3-dimethylamino- vs. 3-aminostilbenes.<sup>16</sup> The aminodihydrophenanthrenes **IIc** and **IId** display large solvent-induced red-shifts in CH<sub>3</sub>CN vs. C<sub>6</sub>H<sub>12</sub> solution and an exceptionally large red-shift is observed for **IIe** (1600 cm<sup>-1</sup>). This shift is nearly as large as that reported for **IIf**, the ring-closed form of the more elaborate diarylethene **If** (eqn. (1),  $\Delta\nu \approx 2000$  cm<sup>-1</sup> in DMSO vs. hexane).<sup>6</sup>



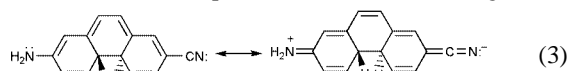
The solvent-induced red-shift for the absorption maximum **IIe** is exceptionally large for an uncharged molecule, indicative of both a large ground state dipole moment and a change in the dipole moment upon electronic excitation. Ground state dipole moments calculated using the INDO/S-SCF-CI (ZINDO) algorithm<sup>22</sup> for **IIa** and **IIc–IIe** are reported in Table 1. The values calculated for **IIc** and **IId** are larger than that for (*E*)-4-dimethylaminostilbene ( $\mu_{\text{g}} = 1.8$  D) and the value calculated for **IIe** is larger than that for (*E*)-4-dimethylamino-4'-cyanostilbene ( $\mu_{\text{g}} = 6.6$  D).<sup>16</sup> The dipole moment of the Franck–Condon excited state ( $\mu_{\text{e}}^{\text{FC}}$ ) may be estimated by using the Lippert equation [eqn. (2)]

$$\bar{\nu}_{\text{a}} = -\frac{2\mu_{\text{g}}(\mu_{\text{e}} - \mu_{\text{g}})}{4\pi\epsilon_0 h c a^3} \Delta f; \Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

where  $\bar{\nu}_{\text{a}}$  is the absorption maximum,  $h$  is Planck's constant,  $\epsilon_0$  is the vacuum permittivity,  $c$  is the speed of light,  $a$  is the radius of the solvent cavity,  $\epsilon$  is the relative permittivity, and  $n$  is the solvent refractive index.<sup>23</sup> Calculated values of  $\mu_{\text{e}}^{\text{FC}}$  for **IIc** and **IId** (Table 1) are larger than that for (*E*)-4-dimethylaminostilbene ( $\mu_{\text{e}}^{\text{FC}} = 7.7$  D)<sup>16</sup> and the calculated value for **IIe** is much larger than that for (*E*)-4-dimethylamino-4'-cyanostilbene ( $\mu_{\text{e}}^{\text{FC}} = 9.0$  D).<sup>12</sup>

The relatively large ground and excited state dipole moments of the aminodihydrophenanthrenes **IIc–IIe** reflect the important

contributions of quinoidal resonance structures to both the ground and excited states [eqn. (3)]. These values are larger than



those for the corresponding 4- or 4'-substituted (*E*)-stilbenes, even though the distance between the donor and acceptor substituents is smaller for the dihydrophenanthrenes. Thus the extent of charge separation must be significantly larger for the dihydrophenanthrenes. Photocyclization of push–pull 4,4'-substituted stilbenes would result in the formation of 3,3'-substituted dihydrophenanthrenes for which quinoidal resonance is not possible. This may explain the absence of reports of photocyclization of these stilbenes. In addition to providing the first example of a simple push–pull stabilized dihydrophenanthrene, these results provide a design principle which may prove useful in the development of new photochromic systems. While the dihydrophenanthrene **IIe** reacts with oxygen, its stability in the absence of oxygen, ease of synthesis and compact molecular structure may provide advantages for **Ie** when compared to more complex photochromic molecules such as **If**.<sup>5,6</sup>

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- Typical experiments used 50  $\mu\text{M}$ –5 mM solutions that were degassed by five freeze–pump–thaw cycles at <0.1 mTorr followed by flame sealing of the cuvet. Irradiation was carried out in a Rayonet RPR-100 photochemical reactor fitted with RPR-3000A bulbs. All UV–Vis spectra were promptly acquired on a Hewlett-Packard HP8452A diode array spectrometer.
- <sup>1</sup>H NMR of **IIIf** (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.08 (d, 2.3 Hz), 7.11 (dd, 8.8, 2.3 Hz), 7.63 (2H, s), 7.74 (dd, 8.6, 1.6 Hz), 8.14 (d, 1.6 Hz), 8.46 (d, 8.6), 8.56 (d, 8.8). **IVe**: 7.08 (d, 2.5 Hz), 7.12 (dd, 8.5, 2.5 Hz), 7.49 (dd, 7.1, 7.6 Hz), 7.61 (2H, s), 7.98 (dd, 7.1, 1.7 Hz), 8.01 (dd, 7.6, 1.7 Hz), 9.59 (d, 8.5 Hz).
- <sup>1</sup>H NMR of **IIc** (300 MHz, CD<sub>3</sub>CN)  $\delta$ : 3.23 (s), 3.27 (s), 5.38 (s), 5.67 (m), 5.77 (m), 5.98 (m), 6.25 (m). Signals of **IIc** downfield from 6.5 ppm were unresolved from those of the *cis* and *trans* isomers of **Ic**.
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