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

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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.1-5 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.^{5,6} 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 (Φ_p) from (Z)-stilbenes in the presence of oxygen was investigated by Güsten and co-workers.^{7,8} They report higher values of $\Phi_{\rm p}$ 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.⁹ 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.^{10–13} 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,^{14–17} 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 (C₆H₁₂) or acetonitrile (CH₃CN) solution promptly followed by acquisition of the absorption spectrum results in the observation of a broad absorption band at long wavelengths.¹⁸ The deconvoluted absorption spectra of IIc, IId, 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 IIIe and IVe in a 4.3:1 ratio, but no detectable 4-amino-7-cyano isomer.¹⁹ 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 CH₃CN solution and undergoes repeated formation and bleaching without degradation. This permits acquisition of the ¹H NMR spectrum of **IIc** as a mixture with **Ic**.²⁰ 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.³ 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.²¹ The absorption bands of **IId** 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_6H_{12} and CH_3CN 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

0.25

0.20 0.15 0.10 0.05 0.00

0.20 0.15

0.10

0.00

200

300

Absorbance 0.00 0.10 0.10 0.00 0.00



† 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, IId, and IIe in acetonitrile solution.

500

Wavelength/nm

600

700

400



800

н Н IId

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

Compd.	λ_{max}/nm (C ₆ H ₁₂)	λ_{max}/nm (CH ₃ CN)	$\mu_{ m g}/{ m D}^a$	$\mu_{\rm e}^{\rm FC}/{\rm D}^{b}$
Ia	276	276		
Ib ^c	277			
Ic ^d	315	320		
Ie	317	328		
IIa ^e	450	450	0.7	0.7
IIb ^e	467			
IIc ^d	470	482	2.4	11.4
IId	482	494	2.1	11.7
IIe	530	578	7.2	16.0
^a Calculated	ground state dip	ole moment. ^b Di	pole moment of	of the Franck-

Condon singlet state calculated using eqn. (2). ^c Data from ref. 8. ^d Data from ref. 17. ^e Data from ref. 3.

to splitting of the long-wavelength band which results from configuration interaction.^{15,16} Much smaller shifts are observed for the 3-cyano substituents in Ib (vs. Ia) and Ie (vs. Ic).9 Also reported in Table 1 are the absorption maxima for the dihydrophenanthrenes IIa-IIe. The substituent-induced redshifts 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.¹⁶ The aminodihydrophenanthrenes **IIc** and **IId** display large solvent-induced red-shifts in CH₃CN vs. C₆H₁₂ solution and an exceptionally large red-shift is observed for IIe (1600 cm⁻¹). This shift is nearly as large as that reported for IIf, the ring-closed form of the more elaborate diarylethene If (eqn. (1), $\Delta v \approx 2000 \text{ cm}^{-1}$ in DMSO vs. hexane).6

The solvent-induced red-shift for the absorption maximum **He** 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) algorithm²² for **Ha** and **Hc–He** are reported in Table 1. The values calculated for **Hc** and **Hd** are larger than that for (*E*)-4-dimethylaminostilbene ($\mu_g = 1.8$ D) and the value calculated for **He** is larger than that for (*E*)-4-dimethylamino-4'-cyanostilbene ($\mu_g = 6.6$ D).¹⁶ The dipole moment of the Franck–Condon excited state (μ_e^{FC}) may be estimated by using the Lippert equation [eqn. (2)]

$$\overline{v}_{a} = -\frac{2\mu_{g}(\mu_{e} - \mu_{g})}{4\pi\varepsilon_{0}hca^{3}}\Delta f; \Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^{2} - 1}{2n^{2} + 1}$$
(2)

where v_a is the absorption maximum, *h* is Planck's constant, ε_0 is the vacuum permittivity, *c* is the speed of light, *a* is the radius of the solvent cavity, ε is the relative permittivity, and *n* is the solvent refractive index.²³ Calculated values of μ_e^{FC} for **IIc** and **IId** (Table 1) are larger than that for (*E*)-4-dimethylaminostilbene ($\mu_e^{FC} = 7.7 \text{ D}$)¹⁶ and the calculated value for **IIe** is much larger than that for (*E*)-4-dimethylamino-4'-cyanostilbene ($\mu_e^{FC} = 9.0 \text{ D}$).¹²

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

$$H_{2}\dot{N} - CN_{1} \leftrightarrow H_{2}\dot{N} = C=N^{-}$$
(3)

those for the corresponding 4- or 4,4'-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.5,6

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Notes and references

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- 18 Typical experiments used 50 μ 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.
- 19 ¹H NMR of **IIIe** (500 MHz, CDCl₃) & 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).
- 20 ¹H NMR of **IIc** (300 MHz, CD₃CN) δ: 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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