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Photochemical synthesis of medium-ring azalactams from *N*-(aminoalkyl)-2-stilbenecarboxamides

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Abstract

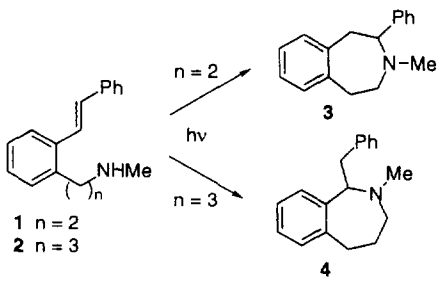
The photochemical reactions of several *N*-(aminoalkyl)-2-stilbenecarboxamides have been investigated. The amine groups quench the stilbenecarboxamide fluorescence intensity, presumably via intramolecular electron transfer. The relatively low quenching efficiencies and the absence of intramolecular exciplex formation are attributed to the molecular structure which prevents effective overlap between the stilbene and amine chromophores. The secondary amines are observed to undergo regioselective intramolecular addition to afford 9- or 10-ring azalactams in 25–43% isolated yield. The dependence of both fluorescence quenching and adduct formation upon molecular structure are discussed.

Keywords: *N*-(aminoalkyl)-2-stilbenecarboxamides; Azalactams; Photochemical synthesis

1. Introduction

Intramolecular photochemical addition reactions provide a versatile method for the construction of medium- and large-ring compounds [1,2]. Intramolecular photoinduced electron transfer between covalently attached donor and acceptor molecules is the initial step in many such reactions. Through-space electron transfer is known to occur with moderate to high efficiency in donor–spacer–acceptor molecules with long flexible spacers and for spacers containing both flexible and rigid elements [3–11]. Coulombic attraction between the resulting radical ion pairs allows them to undergo various reactions, including proton transfer, which result in intramolecular addition.

Several years ago we reported that the intramolecular photoaddition of the *o*-(aminoalkyl)stilbenes **1** and **2** yields the benzazepines **3** and **4**, respectively (Scheme 1) [12]. The mechanism proposed for these reactions is electron transfer from ground state amine to singlet stilbene, followed by proton transfer forming a biradical, which couples to yield the benzazepine. Our interest in synthetic applications of intramolecular electron transfer led us to investigate the photochemical reactions of a series of *o*-stilbene–carboxamides **5**–**12** (Scheme 2). The amide group serves to facilitate synthesis of these donor–spacer–acceptor molecules and to control the conformation of the spacer at the point of its attachment to the acceptor. Both intramolecular quenching of stilbene fluorescence by the covalently attached amines and intramolecular addition to form medium-ring azalactams is found to be dependent upon the length of the alkyl chain and substitution at amine nitrogen.



Scheme 1.

2. Experimental details

2.1. General methods

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using a Gemini 300, Varian VXR-300, or Varian Unityplus 400 spectrometer with TMS as an internal standard. UV–Vis absorption spectra were recorded using a Hewlett-Packard Model 8542A diode array spectrophotometer in 1 cm path length quartz cuvettes. Fluorescence spectra of degassed solu-

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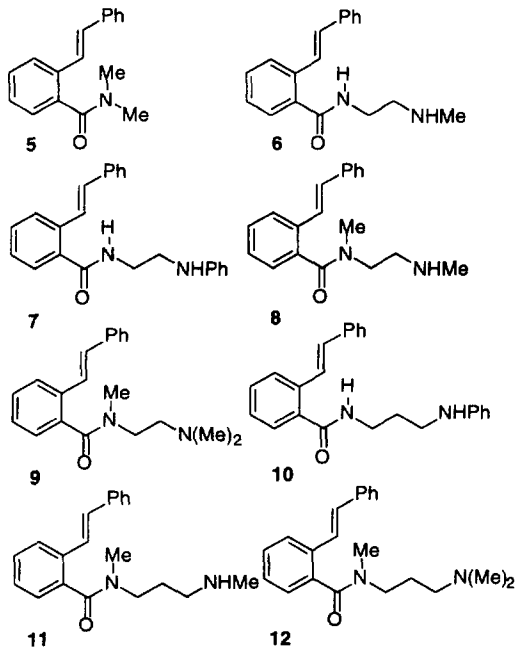


Scheme 2.

tion were recorded with a Spex Fluoromax spectrometer. Photoreactions were carried out by irradiating 10^{-4} M acetonitrile solutions under nitrogen in Pyrex tubes using a Rayonet reactor fitted with 16 RPR 3000 lamps and monitored by gas chromatography with a Hewlett-Packard Model 5890 GC equipped with a 10 m HP-1 (Cross-linked Methyl Siloxane) capillary column. Products were isolated by chromatography on silica gel. Melting points are uncorrected and were determined using a Fisher–Johns melting point apparatus.

2.2. Synthesis of substrates

2.2.1. trans-o-(N,N-Dimethyl)stilbenecarboxamide (5)

The ethyl ester of 2-caboxybenzaldehyde (Aldrich) was reacted with triphenylbenzylphosphonium chloride to afford ethyl *o*-stilbenecarboxylate as a mixture of isomers. This mixture was converted to the pure trans isomer by irradiation with iodine in benzene solution. Refluxing with sodium hydroxide in methanol followed by recrystallization from ethanol yielded *trans-o*-stilbenecarboxylic acid in 80% yield, mp 158–160°C (lit. 159–160°C) [13]. The acid (0.2 g) was converted to its acid chloride by reaction with excess thionyl chloride and the acid chloride dissolved in benzene and cooled in an ice bath. Dimethylamine gas was bubbled into the solution for 10 min and the mixture was stirred overnight at room temperature, then worked up by washing the solution with water, drying over $MgSO_4$ and removing the solvent in vacuo. This afforded **5** as an oil in 76% yield [14]. ^{1}H NMR: δ 7.71 – 7.25 (m, 11H), 3.17 (s, 3H), 2.80 (s, 3H).

2.2.2. trans-o-(N-[2-(N'-Methylamino)ethyl])stilbenecarboxamide (6)

To the acid chloride of *trans-o*-stilbenecarboxylic acid (0.15 g) was added 10 ml of an aqueous solution of 2-bromoethylamine hydrobromide (0.28 g) following the method of Scott et al. [15]. A 0.1 M solution of sodium hydroxide in water was added dropwise and the mixture was stirred for 15 min. The crude product was extracted with chloroform, washed with water, and dried over $MgSO_4$. The solvent was removed in vacuo, and the product was recrystallized from chloroform to give *trans-o*-[*N*-(2-bromoethyl)]stilbenecarboxamide in 46% yield, mp = 144–146°C. ^{1}H NMR: δ 7.71 (d, J = 7.91, 1H), 7.55 – 7.26 (m, 9H), 7.08 (d, J = 16.2, 1H), 6.37 (br s, 1H), 3.86 (m, 2H), 3.59 (t, J = 5.6, 2H). The bromoethylamide (0.19 g) was dissolved in THF (160 ml) and anhydrous methylamine gas was bubbled into the solution for 10 min. The mixture was refluxed overnight. The solvent and excess amine were removed in vacuo, and the product was taken up in chloroform, and washed with water. The solution was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Purification by column chromatography followed by recrystallization with benzene/chloroform afforded **6** in 43% yield, mp 118–120°C. ^{1}H NMR: δ 7.68 (d, J = 7.9 Hz, 1H), 7.53 – 7.25 (m, 9H), 7.05 (d, J = 16.2 Hz, 1H), 6.48 (br s, 1H), 3.54 (m, 2H), 2.78 (t, J = 6.0 Hz, 2H), 2.34 (s, 3H), 1.27 (br s, 1H). ^{13}C NMR: δ 169.64, 137.17, 135.73, 135.55, 131.44, 130.22, 128.74, 127.99, 127.84, 127.55, 126.82, 126.29, 126.19, 50.65, 39.29, 36.04. HRMS: 280.158 (calc.) 280.158 (obsd.).

2.2.3. trans-o-(N-[2-(anilino)ethyl])stilbenecarboxamide (7)

Reaction of *trans-o*-[*N*-(2-bromoethyl)]stilbenecarboxamide with aniline according to the method of Gabriel and Stelzner [16] followed by recrystallization from chloroform gave **7** in 37% yield, mp 147–149°C. ^{1}H NMR: δ 7.68 (d, J = 8.41 Hz, 1H), 7.51 – 7.27 (m, 7H), 7.16 (t, J = 7.5 Hz, 2H), 7.05 (d, J = 16.2 Hz, 1H), 6.72 (t, J = 7.38 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 6.14 (br t, 1H), 4.05 (br s, 1H), 3.74 (m, 2H), 3.40 (t, J = 6.0 Hz, 2H). ^{13}C NMR: δ 170.36, 147.92, 136.91, 135.52, 135.33, 131.69, 130.45, 129.39, 128.87, 128.13, 127.78, 127.62, 126.77, 126.38, 125.89, 117.80, 112.87, 44.57, 39.59. HRMS: 342.173 (calc.) 342.174 (obsd.).

2.2.4. trans-o-(N-Methyl-N-[2-(N'-methylamino)ethyl])-stilbenecarboxamide (8)

To the acid chloride of *trans-o*-stilbenecarboxylic acid (0.15 g) in benzene was added 2 equivalents *N,N'*-dimethylethylenediamine and 10 equivalents of triethylamine. The mixture was stirred overnight at room temperature, then worked up by removing the benzene and excess amines in vacuo, and purifying by column chromatography. This afforded **8** as an orange oil in 63% yield. The ^{1}H NMR spectrum displayed two sets of amide methyl and aminoalkyl signals attributed to the *E* and *Z* conformational isomers and assigned in Table 1. Aromatic protons: δ 7.69 (d, J = 7.97, 1H), 7.50 (t, 2H), 7.39 – 7.07 (m, 8H). ^{13}C NMR: δ 171.42, 137.11, 137.05, 136.20, 135.78, 134.08, 133.87, 131.23,

Table 1
^{1}H NMR chemical shift data for tertiary stilbenecarboxamides [a]

Compound	Amide CH_3	α-CH_2	β-CH_2	γ-CH_2	Amine CH_3
(*Z*)-**8**	2.79 (s)	3.8, 3.55 (b)	2.89 (t)		2.47 (s)
(*E*)-**8**	3.16 (s)	3.19 (b)	2.62 (t)		2.19 (s)
(*Z*)-**9**	2.76 (s)	3.9, 3.45 (b)	2.56 (b t)		2.28 (s)
(*E*)-**9**	3.14 (s)	3.15 (t)	2.28 (b t)		1.95 (s)
(*Z*)-**11**	2.77 (s)	3.67 (b t)	1.88 (m)	2.70 (t)	2.44 (s)
(*E*)-**11**	3.15 (s)	3.15 (b)	1.63 (m)	2.35 (t)	2.23 (s)
(*Z*)-**12**	2.77 (s)	3.60 (b)	1.85 (m)	2.39 (t)	2.23 (s)
(*E*)-**12**	3.15 (s)	3.12 (t)	1.60 (m)	2.02 (t)	2.01 (s)

[a] Chemical shift in $CDCl_3$ solution vs. TMS.

131.17, 129.16, 129.09, 128.93, 128.91, 128.75, 128.31, 128.05, 128.01, 127.80, 127.69, 127.47, 126.79, 126.54, 125.61, 125.35, 125.26, 50.32, 49.47, 49.28, 46.83, 46.12, 37.05, 36.60, 36.23, 32.86. HRMS: 294.173 (calc.) 294.174 (obsd.).

2.2.5. *trans-o-(N-Methyl-N-[2-(N',N'-dimethylamino)-ethyl])stilbenecarboxamide (**9**)*

Reaction of the acid chloride of *trans-o*-stilbenecarboxylic acid with *N,N,N'*-trimethylethylenediamine followed by recrystallized from ethanol/hexane to give **9** as white crystals in 29% yield, mp = 72–73°C. The ^{1}H NMR spectrum displayed two sets of amide methyl and aminoalkyl signals attributed to the *E* and *Z* conformational isomers and assigned in Table 1. Aromatic protons: δ 7.66 (d, J = 7.69, 1H), 7.47 (t, $J \sim 8.5$, 2H), 7.36 – 7.09 (m, 8H). ^{13}C NMR: δ 171.40, 170.94, 137.17, 137.12, 136.30, 135.84, 134.11, 133.83, 131.08, 129.11, 129.03, 128.73, 128.70, 127.98, 127.96, 127.78, 127.56, 126.82, 126.80, 126.75, 126.65, 125.53, 125.42, 125.24, 57.34, 56.66, 48.92, 45.86, 45.58, 45.05, 36.95, 33.07. HRMS: 308.189 (calc.) 308.190 (obsd.).

2.2.6. *trans-o-(N-[3-(anilino)propyl])stilbenecarboxamide (**10**)*

Reaction of the acid chloride of *trans-o*-stilbenecarboxylic acid (0.22 g) with 3-bromopropylamine hydrobromide (0.48 g) afforded *trans-o*-[*N*-(3-bromopropyl)]stilbenecarboxamide in 40% yield, mp 96–100°C. ^{1}H NMR: δ 7.70 (d, J = 7.97, 1H), 7.53 – 7.27 (m, 9H), 7.06 (d, J = 16.2, 1H), 6.02 (br s, 1H), 3.62 (m, 2H), 3.47 (t, J = 6.5, 2H), 2.20 (m, 2H). Reaction of the (3-bromopropyl)-stilbenecarboxamide (0.052 g) with 10 equivalents aniline followed by recrystallization from ethanol/hexane afforded **10** in 93% yield, mp 134–137°C. ^{1}H NMR: δ 7.69 (d, J = 7.48 Hz, 1H), 7.52 – 7.25 (m, 7H), 7.16 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 14.7 Hz, 1H), 6.70 (t, J = 7.32 Hz, 1H), 6.60 (d, J = 7.63 Hz, 2H), 6.03 (br t, 1H), 3.95 (br s, 1H), 3.60 (m, 2H), 3.25 (t, J = 6.5, 2H), 1.90 (m, 2H). ^{13}C NMR: δ 169.93, 136.96, 135.55, 135.49, 131.61, 130.38, 129.36, 128.85, 128.14, 127.68, 127.63, 126.79, 126.39, 125.89, 117.61, 113.08, 41.33, 37.81, 29.39. HRMS: 356.189 (calc.) 356.189 (obsd.).

2.2.7. *trans-o-(N-Methyl-N-[3-(N'-methylamino)-propyl])stilbenecarboxamide (**11**)*

Reaction of the acid chloride of *trans-o*-stilbenecarboxylic acid with *N,N'*-dimethyl-1,3-propanediamine afforded **11** as an oil in 67% yield. The ^{1}H NMR spectrum displayed two sets of amide methyl and aminoalkyl signals attributed to the *E* and *Z* conformational isomers and assigned in Table 1. Aromatic protons: δ 7.70 (m, 1H), 7.48 – 7.22 (m, 8H), 7.10 (s, 2H). ^{13}C NMR: δ 170.92, 166.39, 136.62, 134.21, 132.38, 131.39, 130.00, 129.07, 129.01, 128.81, 128.76, 128.53, 127.94, 127.93, 126.78, 126.72, 126.69, 126.64, 126.59, 126.56, 126.26, 125.68, 125.13, 124.56, 46.83, 44.86, 44.33, 44.28, 37.26, 36.66, 36.10, 33.45, 32.60, 24.03. HRMS: 310.20 (calc.) 310.20 (obsd.).

2.2.8. *trans-o-(N-Methyl-N-[3-(N',N'-dimethylamino)-propyl])-stilbenecarboxamide (**12**)*

Reaction of the acid chloride of *trans-o*-stilbenecarboxylic acid with *N,N,N'*-trimethyl-1,3-propanediamine afforded **12** as an oil in 98%. The ^{1}H NMR spectrum displayed two sets of amide methyl and aminoalkyl signals attributed to the *E* and *Z* conformational isomers and assigned in Table 1. Aromatic protons: δ 7.70 (t, $J \sim 7.4$, 1H), 7.49 – 7.25 (m, 8H), 7.10 (s, 2H). ^{13}C NMR: δ 171.18, 170.90, 137.04, 136.24, 135.92, 133.94, 133.84, 131.24, 131.10, 129.06, 128.78, 128.74, 128.28, 128.03, 127.79, 127.64, 126.78, 126.72, 126.59, 126.46, 125.55, 125.52, 125.20, 125.12, 57.04, 56.64, 49.18, 45.49, 45.44, 45.23, 36.74, 32.54, 26.26, 25.41. HRMS: 324.22 (calc.) 324.22 (obsd.).

2.3. *Characterization of photoproducts*

(**13**) Irradiation of **6** afforded **13** as a colorless oil in 25% isolated yield. ^{1}H NMR: δ 8.12 (m, 1H), 7.35 – 7.19 (m, 5H), 7.08 – 6.97 (m, 3H), 4.94 (dd, J = 2.2, 6.8, 1H), 4.26 (m, 1H), 3.71 (m, 1H), 3.06 – 2.87 (m, 4H), 2.46 (s, 3H). ^{13}C NMR: δ 165.0, 140.09, 135.12, 129.29, 128.67, 127.73,

127.70, 127.66, 127.19, 126.36, 60.37, 50.12, 46.42, 36.21, 35.98. HRMS: 280.158 (calc.) 280.156 (obsd.).

(**14**) Irradiation of **7** afforded **14** as a brown oil in 40% isolated yield. ^{1}H NMR: δ 8.15 (m, 1H), 7.37–6.97 (m, 10H), 6.70 (t, 1H), 6.58 (d, J=7.67, 2H), 4.85 (dd, J=4.18, 6.37, 1H), 4.29 (m, 1H), 3.59 (dd, J=8.79, 15.55, 1H), 3.44 (m, 2H), 3.18 (m, 1H), 3.01 (dd, J=2.55, 15.8, 1H). ^{13}C NMR: δ 165.9, 139.92, 135.09, 132.17, 129.32, 129.08, 128.79, 128.39, 127.84, 127.74, 127.65, 127.26, 126.39, 117.22, 112.49, 60.59, 46.51, 42.98, 35.99. HRMS: 342.173 (calc.) 342.171 (obsd.).

(**15**) Irradiation of **8** afforded **15** as a brown oil in 28% yield. ^{1}H NMR: δ 7.40–7.15 (m, 9H), 4.05 (dd, J~4.0, 11.6, 1H), 3.45 (m, 1H), 3.20–2.95 (m, 4H), 3.13 (s, 3H), 2.45 (m, 1H), 2.25 (s, 3H). ^{13}C NMR: δ 160.5, 129.14, 129.08, 128.40, 128.32, 127.89, 127.85, 127.30, 126.63, 126.30, 68.47, 52.90, 49.48, 43.43, 37.52, 33.79. HRMS: 294.173 (calc.) 294.171 (obsd.).

(**16**) Irradiation of **10** afforded **16** as a colorless oil in 43% isolated yield. ^{1}H NMR: δ 8.15 (m, 1H), 7.37–7.32 (m, 2H), 7.27–7.13 (m, 5H), 7.08–6.98 (m, 3H), 6.70–6.61 (m, 3H), 4.81 (dd, J=2.41, 6.81 Hz, 1H), 4.30 (m, 2H), 3.58 (dd, J=6.6, 15.65 Hz, 1H), 3.28 (m, 1H), 3.19 (m, 1H), 3.03 (dd, J=2.41, 15.9 Hz, 1H), 2.93 (m, 1H), 1.91 (m, 2H). ^{13}C NMR: δ 165.20, 148.18, 139.90, 134.99, 132.07, 129.33, 129.28, 129.23, 128.71, 127.76, 127.64, 127.28, 126.38, 117.08, 112.98, 59.49, 43.82, 40.75, 35.99, 27.26. HRMS: 356.189 (calc.) 356.189 (obsd.).

3. Results and discussion

3.1. Synthesis and structure

The stilbenecarboxamides **5–12** were prepared using standard literature methods as reported in Section 2.2. The acid chloride of *o*-stilbenecarboxamide was either directly reacted with the appropriate diaminoalkane or first reacted with a bromoalkylamine to yield a bromoalkylamide, followed by nucleophilic displacement of bromine by an amine. The tertiary amides **8**, **9**, **11**, and **12** display two sets of ^{1}H NMR signals attributed to the *E* and *Z* conformational isomers. The NMR assignments for these isomers (Table 1) are analogous to those for the 9-phenanthrenecarboxamides previously studied in our laboratory [17,18]. NMR integration indicates that the equilibrium constant for the two isomers is approximately 1.0. The secondary amides **6**, **7**, and **10** have only one set of ^{1}H NMR signals attributed to the *Z* conformational isomers. The tertiary amides are presumed to have larger arene–carbonyl dihedral angles (~90°) than do the secondary amides (~30°) [17].

3.2. Photophysical studies

The absorption and fluorescence spectra of the stilbenecarboxamides **5–12** are similar to those of *trans*-stilbene [19]. The amide substituent in **5** causes a small red-shift in both the absorption maximum (298 vs. 295 nm for stilbene) and fluorescence maximum (352 vs. 348 nm for stilbene) and broadening of both spectra in hexane solution. The fluorescence quantum yield of **5** (0.013) is lower than that of stilbene (0.050) [19] in hexane solution. The singlet lifetime is also presumably shorter than that of stilbene (0.11 ns) [19], but is too short to measure with our single photon counting apparatus, which has a time resolution of ~0.2 ns. Carbonyl-containing substituents are commonly observed to decrease the singlet lifetimes of aromatic hydrocarbons, plausibly due to mixing of the lowest arene π,π^* state with the carbonyl n,π^* state [17,20]. Nonbonded interaction between the stilbene double bond and *o*-carboxamide group might also lower the barrier for twisting about this bond.

Quantum yields for fluorescence (Φ_f) of the stilbenecarboxamides relative to that of **5** in acetonitrile solution are reported in Table 2. The reduction in Φ_f for the (aminoalkyl)-stilbenecarboxamides **6–12** is attributed to intramolecular electron transfer quenching of the singlet stilbene by the covalently appended amine. The extent of quenching ranges from 76% for **7** to 9% for **12** and is lower in solvents less polar than acetonitrile (e.g. hexane or benzene). Intramolecular quenching by the aminoalkylcarboxamides is less efficient than is observed for the (aminoalkyl)stilbenes **1** and **2** and for their tertiary amine analogues [12]. This decrease in quenching efficiency may reflect the decrease in singlet lifetime for the *o*-stilbenecarboxamides vs. *o*-alkylstilbenes and/or less efficient through-bond and through-space interactions of the stilbene and amine groups in the (aminoalkyl)-stilbenecarboxamides. Less efficient quenching for the aminopropyl- vs. aminoethylamides (Table 2) suggest a likely role for through-bond interactions. More efficient quenching for the aniline vs. methylamino compounds is consistent with the lower oxidation potentials of anilines vs. alkylamines [17]. The secondary amines **6** and **11** are more efficient quenchers than are their tertiary analogues **8** and **12**, in spite of the higher oxidation potentials for secondary vs. tertiary amines. The formation of intramolecular adducts for secondary but not tertiary amines suggests that electron and proton transfer may be coupled processes in the case of quenching by secondary amines.

No exciplex fluorescence is observed for the (aminoalkyl)carboxamides. Exciplex fluorescence is generally not observed for arene-secondary amine exciplexes; however, we previously observed exciplex fluorescence for the tertiary (aminoalkyl)stilbene analogues of **1** and **2**. The absence of exciplex fluorescence for the **9** and **12** may reflect the rigid nature of the amide group which prevents the short-chain aminoalkyl group from folding over the face of the stilbene. Vanderawerera et al. [6] have reported the observation of intramolecular exciplex fluorescence for (aminoalkyl)-2-anthracenecaboxylates with long-chain alkyl groups (9 or 11 carbons) but not with short-chain alkyl groups (2, 3 or 5 carbons). Similarly, no exciplex fluorescence is observed for (aminoalkyl)-9-phenanthrenecarboxamides with short-chain alkyl groups (2 or 3 carbons) [17].

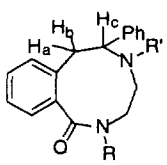
Table 2
Fluorescence quantum yields and adduct yields for stilbenecarboxamides

Compound	Φ_f [a]	Adduct yield, % [b]
5	1.0	
6	0.53	25
7	0.24	40
8	0.51	28
9	0.84	none
10	0.56	43
11	0.71	none
12	0.91	none

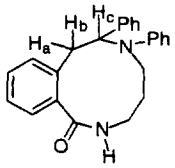
[a] Fluorescence intensity relative to that for **5** in acetonitrile solution.
[b] Isolated yield of intramolecular adduct formation irradiated in acetonitrile solution.

3.3. Intramolecular photoaddition

Irradiation of **5** in acetonitrile solution results in isomerization to yield a steady-state mixture of *trans* and *cis* isomers. The (aminoalkyl)stilbenecarboxamides **6–12** undergo photoisomerization with efficiencies similar to that of **5**. The failure of fluorescence quenching to result in inhibition of photoisomerization was also observed for the (aminoalkyl)stilbenes and attributed to exciplex intersystem crossing to yield the locally excited stilbene triplet [12]. Prolonged irradiation of **6–8** and **10** results in the formation of the adducts **13–16** in yields ranging from 25–43%. The adducts account for the only significant product peaks other than residual trans and cis starting material observed in the gas chromatograms of irradiated solutions or in the NMR spectra of non-chromatographed product mixtures. The structure assignments are based primarily upon analysis the ^{1}H NMR spectra for the three benzyl protons H_a–H_c of **13–16**. For example, in the case of **16** these protons appear as a first order AMX spectrum: the doublet of doublet at 4.81 is assigned to H_c and those at 3.58, and 3.03 ppm are assigned to H_a and H_b. The large difference in chemical shift for H_a and H_b is inconsistent with the alternative 9-membered lactam, for which the two exocyclic benzylic protons would be expected to have similar chemical shifts. The ^{1}H NMR spectra for the three benzyl protons of **13** and **14** are almost identical to that of **16**. The spectrum of **15** is less well resolved and thus cannot be assigned with the same level of certainty.



13 R = H, R' = Me
14 R = H, R' = Ph
15 R = Me, R' = Me



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The adducts **13–16** are assigned structures which are consistent with N–H transfer to the proximal end of the stilbene double bond followed by C–N bond formation at the distal end of the double bond. The formation of **3** also occurs via N–H transfer to the proximal end of the stilbene double bond; however **4** must be formed via N–H transfer to the distal end of the double bond (Scheme 1). The conformational preferences of the benzamide and *o*-styryl groups may preclude distal N–H transfer in the case of the stilbenecarboxamides.

Adduct formation is dependent upon amine substitution and the aminoalkyl chain length. No adduct formation is observed for the tertiary amines **9** and **12**. Stilbenes and tertiary amines are known to undergo intermolecular but not intramolecular photoaddition [2,12]. Differences in exciplex conformation may be responsible for the occurrence of inter- but not intra-molecular addition. Higher yields of adduct formation are observed for the anilines **7** and **10** compared to the methylamines. This difference is particularly noticeable in the case of the aminopropyl compounds, the methylamine **11** failing to form an adduct. Evidently, secondary anilines are more reactive than methylamines in both the electron transfer quenching and proton transfer steps of the addition process. The reactivity of secondary anilines has been exploited by Sugimoto et al. [21] in their studies of intramolecular photoaddition reactions of ((*N*-phenyl)aminoalkyl)phenanthrenes.

In summary, intramolecular photoaddition of several (aminoalkyl)-2-stilbenecarboxamides provides a convenient method for the synthesis of 9- and 10-ring azalactams. While the yields of photochemical addition are only fair, the formation of a single regioisomer facilitates product isolation. Based on the observation of more efficient intramolecular exciplex formation for (aminoalkyl)-2-anthracenecarboxylates with long-chain vs. short-chain aminoalkyl groups [6], it is possible that stilbenecarboxamides with long-chain secondary aminoalkyl groups might undergo efficient intramolecular addition to yield macrocyclic azalactams. Separation of the stilbene and amide groups with a second polymethylene spacer might also facilitate intramolecular exciplex formation and addition. Griesbeck et al. [22] have reported the photochemical synthesis of large-ring lactams from amide-linked *ω*-phthalimidoalkanoates. We have observed intramolecular exciplex formation from amide-linked (aminoalkyl)styrenes and report their intramolecular photoaddition reactions in the accompanying article [23].

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