Exciplex Conformational Control of Intramolecular Photoaddition Regioselectivity

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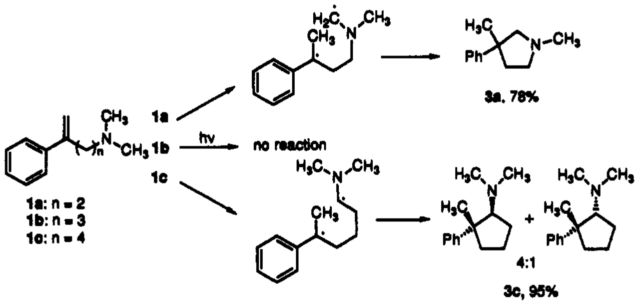
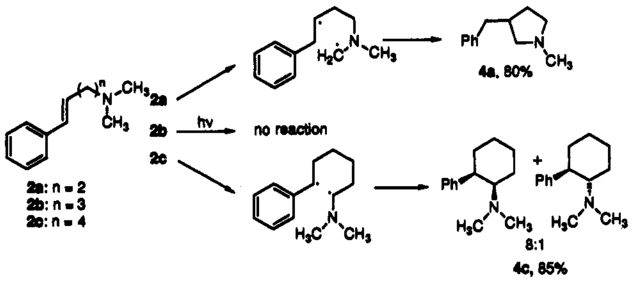
The formation and photophysical behavior of intramolecular exciplexes in which the electron donor and acceptor are connected by a flexible polymethylene chain have been the subject of numerous investigations.[1–6] The stability, polarity, and lifetime of the resulting exciplexes are dependent upon the polymethylene chain length.[1–3] Based upon their extensive experimental and computational studies of ((*N*,*N*-dimethylamino)alkyl)arene singlet exciplexes, De Schryver, Van der Auweraer, and co-workers[3,4] have suggested that in nonpolar solvents these exciplexes adopt specific compact folded conformations which maximize Coulombic attraction while minimizing nonbonded interactions in the polymethylene chain. Whereas the conformation of chemically reactive exciplexes might also be expected to control the regioselectivity of intramolecular addition reactions, we are unaware of any experimental studies which directly relate the conformation of fluorescent intramolecular exciplexes to their chemical behavior. We report here the preliminary results of our investigation of the photochemical behavior of ((*N*,*N*-dimethylamino)alkyl)styrenes in which the aminoalkyl group is attached to the styrene α- or β-carbon with a two-, three-, or four-methylene chain. The (aminoethyl)- and (aminobutyl)styrenes undergo efficient intramolecular addition via fluorescent exciplex intermediates, while the (aminopropyl)styrene exciplexes are unreactive. Rate constants for proton transfer are dependent upon the length of the polymethylene chain, the point of attachment (α vs β), and solvent polarity. These results serve to establish the relationship between exciplex conformation and product formation.

The α- and β-(aminoalkyl)styrenes **1a–c** and **2a–c** (Schemes I and II) were prepared by standard synthetic procedures.[7–9] Irradiation of **1a** (254 nm, hexane solution) results in the formation of **3a**, as previously reported by Aoyama et al.[8] A 1,5-biradical intermediate formed upon regioselective hydrogen transfer from an *N*-methyl group to styrene C_β is the presumed precursor of **3a** (Scheme I). Prolonged irradiation of **1b** under similar conditions results in low conversions to several unidentified products. Irradiation of **1c** in hexane solution results in the efficient formation of **3c** as a 4:1 mixture of diastereoisomers. The presumed precursor of both diastereoisomers is the 1,5-biradical formed via transfer of a methylene C–H to styrene C_β (Scheme I). The photochemical behavior of the β-(aminoalkyl)styrenes is analogous to that of the α-(aminoalkyl)styrenes in that **2a** and **2c** undergo efficient intramolecular addition to yield **4a** and **4c** (8:1 mixture of diastereoisomers), respectively, while **2b** is stable to prolonged irradiation. The presumed precursors of **4a** and **4c** are the 1,5-biradical and 1,6-biradical, respectively, formed upon regioselective hydrogen transfer from an *N*-methyl group to styrene C_α in **2a** and upon hydrogen transfer from the *N*-methylene to styrene C_β in **2c** (Scheme II).

Scheme I



Scheme II



Quantum yields for product formation measured at low conversions on an optical bench using 281-nm irradiation are reported in Table I. Quantum yields decrease with increasing solvent polarity, as previously reported for **1a** by Aoyama et al.[8] The ratio of diastereomers from **1c** is the same in hexane and ether solution. The very low quantum yields for product formation in acetonitrile solution are consistent with our previously reported failure to detect product formation from **1b** or **2b** in this solvent.[9] All of the (aminoalkyl)styrenes display very weak, short-lived styrene fluorescence ($\tau < 0.1$ ns for **1a** and 0.15 ns for **2a**[9]) indicative of highly efficient and largely irreversible intramolecular electron-transfer quenching of styrene singlets by ground-state amine. All of the (aminoalkyl)styrenes except **2c** display exciplex fluorescence in nonpolar solvents. Lifetimes for exciplex fluorescence are reported in Table I.

The intermolecular addition reactions of singlet styrenes[10] and stilbenes[11] with tertiary amines have been assumed to occur via a singlet exciplex mechanism; however, this mechanism has been challenged by Aoyama et al.[8] on the basis of different extents of quenching of exciplex fluorescence and product formation from

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(7) The syntheses of **1a**[8] and **2a–c**[9] have been reported as has the structure of **3a**.[8] Structures of all new reactants and products are based upon ^{1}H NMR and mass spectroscopy. Product yields are based on GC analysis of preparative irradiations at high conversions of reactant (aminoalkyl)styrenes (>95%). Details will be reported subsequently.

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Table I. Quantum Yield and Lifetime Data for (Aminoalkyl)styrenes

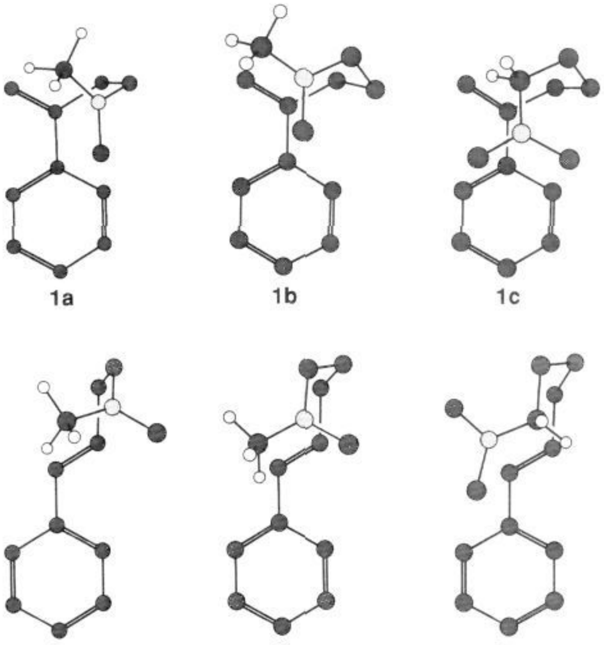
styrene	solvent	Φ_{add}[a]	$\tau_{\mathrm{e}}x$,[b] ns	$10^{-8}\,k_{\mathrm{H}}$, s^{-1}
1a	C_6H_{14}	0.19	0.46	4.1
	$(CH_3CH_2)_2O$	0.05	1.1	0.45
	CH_3CN	<0.01	3.1	<0.03
1b	C_6H_{14}	<0.01	5.6	<0.02
	CH_3CN	<0.01	2.5	<0.01
1c	C_6H_{14}	0.20	1.2	1.7
	$(CH_3CH_2)_2O$	0.06	5.3	0.11
	CH_3CN	<0.01	*c*	
2a	C_6H_{14}	0.07	2.2	0.3
2b	C_6H_{14}	<0.01	3.5	<0.03
2c	C_6H_{14}	0.21	*c*	

[a] Quantum yield for product formation in 0.01 M deoxygenated solution measured using 281-nm irradiation at <10% conversion. [b] Lifetime of exciplex fluorescence for deoxygenated solutions determined by single photon counting. [c] Exciplex fluorescence not detected.

1a by added biacetyl. They suggested that formation of the fluorescent exciplex and product formation are competing rather than consecutive processes. We have investigated the quenching of exciplex fluorescence and product formation from both **1a** and **2a** by propylamine[12,13] and find that the slopes of linear Stern–Volmer plots for quenching by 0.05–0.2 M propylamine in hexane solution are the same, within the experimental error.[14] This result is consistent with the recent report by Miyasaka et al.[6b] that intramolecular photoreduction of triplet benzophenone by a linked diphenylamine occurs predominantly via a sequential electron-transfer, protron-transfer mechanism. Confirmation of a singlet exciplex mechanism for intramolecular addition of the (aminoalkyl)styrenes allows calculation of the rate constants for intramolecular proton transfer from the quantum yield and exciplex lifetime data (Table I, $k_{\mathrm{H}} = \Phi_{\mathrm{add}}\tau_{\mathrm{ex}}^{-1}$).

De Schryver and Van der Auweraer[4] have proposed that fluorescent ((*N*,*N*-dimethylamino)ethyl)arene exciplexes adopt a compact, folded conformation in nonpolar solvents in which the ethane C–C bond is nearly eclipsed so as to position the nitrogen above the arene plane near the ipso carbon. Analogous conformations for the exciplexes of **1a** and **2a** would place an *N*-methyl hydrogen above the styrene C_β in **1a** and styrene C_α in **2a** (Chart I).[15] Least motion pathways for 1,6-proton transfer lead to the 1,5-biradical intermediates shown in Schemes I and II. The singlet exciplexes of ((*N*,*N*-dimethylamino)propyl)arenes are proposed to adopt a folded g^+g^- conformation in which nitrogen lies beyond the ipso carbon toward the center of the aromatic ring.[4] Analogous conformations for **1b** and **2b** would place the *N*-methyl hydrogens beyond the styrene C_β in **1b** and styrene C_α in **2b**. The absence of a least motion pathway for 1,7-proton transfer in these exciplexes may account for their lack of reactivity and longer exciplex lifetimes. Finally, the ((*N*,*N*-dimethylamino)butyl)arene exciplexes are proposed to adopt a folded $g^+g^-g^-$ conformation in which nitrogen lies near the center of the aromatic ring.[4] Analogous conformations for **1c** and **2c** would place a *N*-methylene hydrogen above the styrene C_β in both **1c** and **2c**. Least motion pathways for 1,6-proton transfer in **1c** and 1,5-proton transfer in **3c** would lead to the 1,5- and 1,6-biradical intermediates shown in Schemes I and II.

Chart I



1a **1b** **1c**

2a **2b** **2c**

The rate constants for intramolecular exciplex proton transfer for **1a** and **1c** decrease markedly with increasing solvent polarity (Table I). This decrease may be indicative of a looser exciplex geometry in more polar solvents, as previously proposed for nonreactive intramolecular arene–amine exciplexes.[5,6] A looser geometry would be expected to be less favorable for intramolecular proton transfer. In contrast, the quantum yield for intermolecular addition of singlet styrenes with tertiary amines is not highly dependent upon solvent polarity.[9,10] The loose geometries available to intramolecular exciplexes may not be available to intermolecular exciplexes which, unlike intramolecular exciplexes, can undergo ionic dissociation in polar solvents.[6] The increase in exciplex lifetime for **1a** and **1c** with increasing solvent polarity results at least in part from a decrease in the rate constant for proton transfer and may also reflect the effects of solvation on the exciplex radiative and nonradiative decay rate constants.[5,6]

Both the rate constant and the regioselectivity of intramolecular exciplex proton transfer are dependent upon the chain length and point of attachment of the aminoalkyl group. The significantly larger proton-transfer rate constant for **1a** vs **2a** may reflect the greater basicity of C_β vs C_α in the styrene anion radical. Intramolecular exciplex proton transfer from tertiary amines to styrenes occurs exclusively to styrene C_β.[9,10] The rate constants for **1a** and **1c** are more nearly similar, as might be expected since both reactions involve 1,5-proton transfer to styrene C_β. In comparison to these results, the intramolecular N–H addition reactions of the analogous secondary (aminoalkyl)styrenes display much lower chain length dependence, regioselectivity, and solvent dependence.[9] The absence of either exciplex fluorescence or selective quenching of product formation by added primary amines suggests that N–H addition of secondary amines has a much lower activation energy than C–H addition of tertiary amines, in accord with the failure of C–H addition to compete with N–H addition in secondary amines.

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(12) Unlike biacetyl, which is a competitive absorber and quenches both singlet styrene and its exciplex, primary amines are not competitive absorbers and are known to be more efficient quenchers of fluorescent intermolecular arene–tertiary amine exciplexes than of singlet arenes.[13]

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(14) The exciplex lifetime and Stern–Volmer constants provide a rate constant for exciplex quenching of 2.2×10^{10} M^{-1} s^{-1}. The rate constant for quenching of 1-phenylpropene by propylamine is 3.6×10^{8} M^{-1} s^{-1}.

(15) The structures shown in Chart I were obtained using Chem 3D Plus assuming standard ground-state bond lengths and bond angles except for nitrogen, which is assumed to be planar rather than pyramidal. Torsional angles have been adjusted to attain folded conformations whose energies have not been minimized.