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Photoinduced Through-Bond Electron Transfer and Rearrangement in Bichromophoric Chain Molecules

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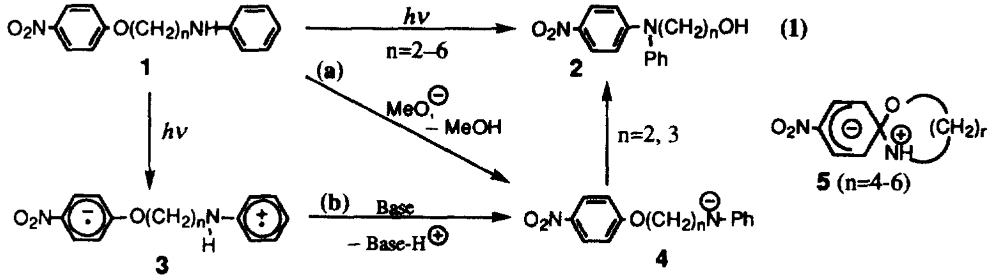
Abstract: Relative quantum yields for the intramolecular electron transfer in *N*-[ω-(*p*-nitrophenoxy)alkyl]anilines **1** and the analogues are determined. The role of through-bond and through-space pathways in the photorearrangement of **1**(n=2-6) is discussed in connection with the quantum yields of the reaction in acetonitrile and benzene.

Through-bond electron transfer (ET) is a well documented process,$^{1)}$ but there have been reported few cases in which the process results in *intramolecular* chemical reactions.$^{2)}$ This may be due to the difficulty of finding an appropriate donor/acceptor couple which undergoes, upon irradiation, transformation into a radical ion pair with newly developed reactive centers that combine to give a sufficiently stable end product. Since the photorearrangement of **1**(n) (Eq. 1) is a clean reaction, showing versatile chain-length dependent reactivities and solvent effects, this reaction is suitable as a model for the study of the relationship of the efficiency of the through-bond ET and the reactivity (fate of the radical ion pair).



The objectives of the present letter are to study (1) the chain-length dependence of the quantum yield of the rearrangement, (2) the effects of solvents and a base-catalyst on the reaction, and (3) the relative significance of through-bond and through-space ET processes in the reaction.

Upon irradiation of the lower homologues (n=2-6) of **1** with 313-nm light, corresponding to the λ_{max} of the *p*-nitrophenoxy group, compound **2** is obtained as a sole product. A radical ion pair **3** has been established to be a reaction intermediate by laser flash photolysis.[3] The generation of **3** takes place through an intramolecular ET process induced by excitation of the aromatic acceptor group. Along with this photoreaction, **1** thermally undergoes the same rearrangement in the presence of a strong base such as sodium methoxide, though the reaction is limited only to the n=2 and 3 homologues (path a).[4] In the presence of a weak base such as pyridine, the thermal reaction did not take place, but irradiation of an acetonitrile solution containing the base reveals remarkable acceleration of the reaction (the order of the quantum yield, n=2>3>4>5>6),[5] though the effect is again limited to the lower two homologues (Table 1). Thus, the role of the base in this solvent is to abstract a proton from the radical cation of the anilino moiety to give an anilide anion **4** as a second intermediate (path b).

Table 1. Quantum Yields for the Photorearrangement of 1

	Number of Methylene Groups, n				
Solvent System[a]	2	3	4	5	6
CH_3CN	0.00004	0.00008	0.013	0.0042	0.00015
CH_3CN + Pyridine	0.14	0.024	0.013	0.003	0.0002
C_6H_6	0.055	0.004	0.076	0.0015	>0
C_6H_6 + Pyridine	0.070	0.054	0.085	0.012	

a) Concentrations of 1 and pyridine are 1×10^{-4} and 0.10 *M*, respectively.

Consistent with this base-catalysis mechanism, the reactivity of the longer chain homologues **1**(n=4-6) is insensitive to the presence of the base, suggesting that the anion **4**(n≥4) cannot lead to the product **2**. In the absence of the base, the reaction in acetonitrile revealed quite a different order of the quantum yield, n=4>5>6>2,3. In this solvent system, the reactivity of the lower homologues is extremely low and that of the higher homologues is relatively high. A possible mechanism for these higher homologues (n=4-6) is direct intramolecular cyclization of **3** (that is, radical recombination) to yield a spiro-Meisenheimer type complex **5**, followed by decomposition into **2**. This mechanism is consistent with the base-catalysis effect described above, but the driving force to ease the formation of less accessible medium-sized ring complexes still remains unknown.

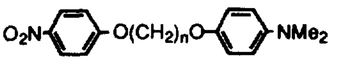
In order to gain further insight into the reaction mechanism, we determined the relative quantum yields of the charge separation (Φ_{ET})[6] and the lifetimes of the resulting radical ion pair (τ_{RIP}) of **1** as well as those of the analogues, with a different donor **6** and with a pair of an acceptor and a donor fixed at 1- and 4-positions of a cyclohexane ring, **7** and **8**.[7] The results obtained for acetonitrile solutions are summarized in Table 2. It should be noted that an excited singlet nitro-aromatic chromophore generally undergoes a rapid intersystem crossing to the triplet. Hence, the radical ion pair **3** is in the triplet state, and the intersystem crossing to the singlet state is required before the radical pair either yields the Meisenheimer complex or decays to the ground state.

The relative quantum yields for the cyclohexane derivatives, **7** and **8**, are higher than those of the corresponding four-methylene counterparts, **1**(4) and **6**(4), irrespective of the stereoisomerism. Since the through-bond ET is the only possible process in these rigid model compounds, the results show the inferiority of the flexible methylene chain as a medium for ET to the rigid σ-bond framework in the cyclohexane counter-

Table 2. Relative Quantum Yields for Radical Ion Pair in Flexible and Rigid Model Compounds in Acetonitrile

Compounds		Rel. Quantum Yield[a]	Compounds	Rel. Quantum Yield[a]
1	n=2	1.00 (81)[b]		
	3	1.29 (110)	*cis*-**7**	1.99 (560)[b]
	4	1.08 (220)	*trans*-**7**	1.55 (310)
	5	0.65 (120)		
	6	0.32 (130)		
6	n=2	1.75 (96)		
	3	0.99 (160)	*cis*-**8**	1.56 (600)
	4	0.90 (95)	*trans*-**8**	1.37 (670)
	6	0.38 (61)		

a) The absorbance of 1(2) is set as a standard. b) Figures in parentheses are lifetimes in ns.



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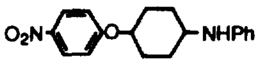

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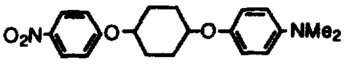

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part. The flexibility of the chain provides a chance for the close approach of the chromophores, which decreases with the chain length. Thus, both the through-space and through-space ET contribute to the generation of the radical anion in **1** and **6**. Probably the large value of **6**(2) is largely due to the through-space process. However, considering that intramolecular charge-transfer interaction in **1**, a typical phenomenon indicating π–π overlap of the chromophores, has been observed only in the shorter chain homologues (n=2,3),[8] the above finding suggests that the through-space ET is a minor mechanism in the longer chain (n≥4) homologues of **1** and **6** and the through-bond ET plays a major role. The smaller Φ_{ET} for **1**(2) (and probably **1**(3)) may be due to the presence of an effective and rapid charge recombination process from a singlet intramolecular exciplex, plausibly formed in these homologues.

Another noticeable feature of the cyclohexane derivatives is the much longer lifetime of the radical ion pair; for instance, 600-670 ns for **8** in contrast to 96 ns for **6**(4). Stabilization of the highly polar species by solvent reorganization may retard the charge recombination process. On the other hand, flexibility of the chain in **1** seems to help the decay partly by a pathway to the reaction and partly by back ET. A decrease of τ_{RIP} for the n=5 and 6 homologues of **1** and **5** may be explained by an increase of the intersystem crossing rate owing to the decrease of exchange interaction of the farther separated triplet radical pairs, because the interaction decreases as the distance of the radical centers increases. The observed short lifetimes for the n=2 homologues of both the reacting and the non-reacting systems, **1** and **6**, suggest the presence of a fast decay pathway overcoming the larger exchange interaction (smaller chance of intersystem crossing) to the ground state in the short chain molecules.

The high quantum yields of the reaction observed in benzene solution are somewhat perplexing (Table 1). Since the radical ion pair is less stable in a nonpolar solvent than in acetonitrile, we expected smaller Φ_{ET}'s and, hence, far less or no reactivity for all the homologues in this solvent. However, a catalytic effect of pyridine, found to be remarkable in 1(3) and 1(5) and to a lesser extent in 1(2) and 1(4), indicates generation of a polar species with an acidic N-H hydrogen atom; that is, the radical ion pair **3** or an exciplex. In nonpolar solvents, through-bond ET and exciplex formation have been observed by fluorescence spectroscopy9) and in photoreactions.10) In the present case, however, no absorption spectrum assignable to **3** was detected. This is probably due to a fast decay of **3**,11) exceeding the time resolution of our apparatus ($\tau_{RIP} \geq 10$ ns).7) A remarkable fluorescence quenching effect of the *p*-nitrophenoxy group observed for the homologues (n=2-6) of *p*-$O_2NC_6H_4O$-$(CH_2)_n$-NH-1-Naphthyl in a benzene-cyclohexane solution may be cited as supporting evidence for this explanation.12) The high quantum yields in benzene may be due to a high reactivity of the poorly solvated intermediate species.

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