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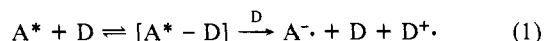
**Supplementary Material Available:** Tables of final fractional coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors for **1** (42 pages). Ordering information is given on any current masthead page.

## Chemistry of Exciplexes. 19. Exciplex-Promoted Electron Transfer in 1-(Phenylamino)-3-(9-anthryl)propanes

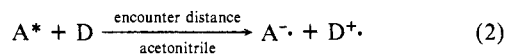
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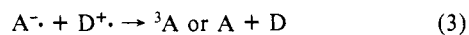
Light-induced electron transfer in multicomponent systems and polychromophoric molecules is a subject of current interest.<sup>4-10</sup> In nonpolar media, a photoexcited molecule may react with a ground-state molecule in a specific orientation yielding an exciplex which may be characterized by its fluorescence.<sup>11</sup> Exciplexes may be deactivated by another ground-state molecule, and it has been suggested that electron transfer may play a role in this deactivation (e.g., reaction 1 where A\* is an excited acceptor and



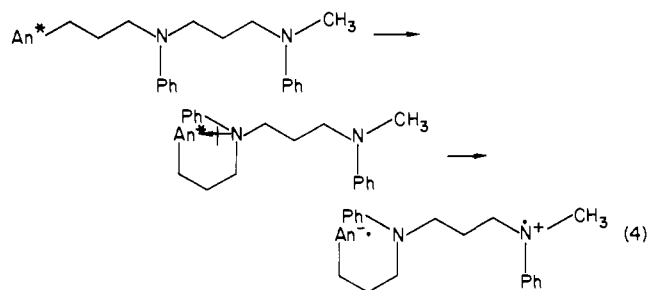
D is a donor).<sup>4-9</sup> However, this suggestion was not supported by any direct experimental evidence. A photoexcited molecule may react with a ground-state molecule to undergo electron transfer at an encounter distance yielding a radical ion pair in polar media (e.g., reaction 2).<sup>11</sup> These radical ions tend to undergo rapid back



electron transfer to revert back to substrates in their ground state or triplet state (e.g., reaction 3).<sup>12,13</sup> In order to convert light



energy into chemical energy in an efficient manner, the rate of back electron transfer must be controlled or retarded. In this investigation, we examined the reactive intermediates generated from photoexcited polychromophoric systems by kinetic spectroscopy. The compounds used were **1-3** containing an anthryl group as the photoexcited acceptor and one or two dialkylanilino groups as the donor(s).<sup>4,14-16</sup> The intermediates derived from these



photoexcited compounds, the anthryl radical anion, dialkylanilino radical cation, and anthryl triplet all exhibit well-defined absorption characteristics.<sup>17-19</sup> This paper demonstrates that an exciplex may undergo electron transfer with another donor molecule in dichloromethane and the lifetimes of ions generated in such a system are substantially longer than the lifetimes of ions from analogous electron transfers in polar media.

Nanosecond transient absorbance measurements were performed with a spectrometer of conventional design, utilizing a frequency tripled Nd-YAG laser.<sup>20</sup> The laser generates a 355-nm, 5-mJ, and 5-ns (fwhm) pulse at 10 Hz which determines the limiting time resolution for the measurements. Similar experiments were performed on a picosecond time scale using a dual beam spectrometer employing multichannel detection. A 600-nm, 2.5-mJ and 2-ps (fwhm) pulse at 10 Hz frequency doubled to yield a 140-μJ pulse at 300 nm. The residual 600-nm light was focused into a cell containing D<sub>2</sub>O to generate the picosecond white light pulse used in the spectroscopic measurements.<sup>21</sup> Solutions containing 5 × 10<sup>-4</sup> M of the samples were circulated through a 1-mm cuvette at a rate sufficient to ensure the excitation of a new sample for each pulse from the laser. The formation and decay of the anilino radical cation as well as that of the anthryl anion were monitored at 470<sup>17</sup> and 700 nm,<sup>18</sup> respectively. The formation of anthryl triplet was monitored at 425 nm.<sup>19</sup> The data were collected and analyzed with a PAR OMA-II detector controlled by a DEC LSI-11/73 computer. The results are tabulated in Table I.

The data from Table I clearly demonstrate that the properties of photoexcited **1** and **2** in acetonitrile, a polar solvent, are practically identical, while those of **3** are in agreement with previous findings.<sup>22-24</sup> All these compounds exhibit extremely rapid rises in absorption of the order of 5-10 ps in the regions where radical ions absorb followed by a rapid decay to form either the ground state or the triplet state of the substrate (270 ps-2.5 ns).<sup>25</sup> However, the properties of photoexcited **1** in dichloromethane differ from those of **2** in that **1** undergoes electron transfer to generate radical ions while **2** does not. Photoexcited **2** exhibits an appreciable exciplex fluorescence (λ<sub>max</sub> 530 nm, φ<sub>f</sub> 0.12, τ<sub>f</sub> 28 ± 1 ns) in deaerated dichloromethane. Although photoexcited **2** also yields a broad and weak absorption at 700 nm, it decays with the same lifetime as that of the exciplex which corresponds to the risetime of the anthryl triplet absorption. The results indicate that the exciplex from **2** undergoes intersystem crossing without passing through the intermediate stage of radical ions. Photoexcited **1** exhibits a very weak exciplex fluorescence (λ<sub>max</sub>

- (1) University of Chicago.  
(2) National Science of Foundation Predoctoral Fellow, 1984-1985.  
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(4) Larson, J. R.; Petrich, J. W.; Yang, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 5000.  
(5) Yang, N. C.; Shold, D. M.; Kim, B. *J. Am. Chem. Soc.* **1976**, *98*, 6587.  
(6) Hub, W.; Schneider, S.; Dörr, F.; Oxman, J. D.; Lewis, F. D. *J. Am. Chem. Soc.* **1984**, *106*, 701, 709.  
(7) Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870.  
(8) Mataga, N.; Karen, A.; Okada, T.; Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1984**, *88*, 5138.  
(9) Saltiel, J.; Townsend, D. E.; Watson, B. D.; Shannon, P.; Finson, S. L. *J. Am. Chem. Soc.* **1977**, *99*, 884.  
(10) Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L. *Nature (London)* **1984**, *307*, 630.  
(11) Weller, A. *Pure Appl. Chem.* **1982**, *54*, 1885.  
(12) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129.  
(13) Mataga, N. *Radiat. Phys. Chem.* **1983**, *21*, 83.  
(14) (a) Hamann, H.-J.; Pragst, F.; Jugelt, W. *J. Prakt. Chem.* **1976**, *318*, 369. (b) Yang, N. C.; Neoh, S. B.; Naito, T.; Ng, L.-K.; Chernoff, D. A.; McDonald, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 2806.  
(15) Chuang, T. J.; Cox, R. J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1974**, *96*, 6828.

- (16) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 2233.  
(17) Potashnik, R.; Goldschmidt, C. R.; Ottolenghi, M.; Weller, A. *J. Chem. Phys.* **1971**, *55*, 5344.  
(18) Shida, T.; Nosaka, Y.; Kato, T. *J. Phys. Chem.* **1978**, *82*, 695.  
(19) Birks, J. B., Ed. "Organic Molecular Photophysics"; Wiley: New York, 1975; Vol. 1, pp 313, 341.  
(20) Wasielewski, M. R.; Norris, J. R.; Bowman, M. K. *Faraday Discuss. Chem. Soc.*, in press.  
(21) Wasielewski, M. R.; unpublished results.  
(22) Migita, M.; Okada, T.; Mataga, N.; Nakashima, N.; Yoshihara, K.; Sakata, Y.; Misumi, S. *Chem. Phys. Lett.* **1980**, *72*, 229.  
(23) Crawford, M. K.; Wang, Y.; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *79*, 529.  
(24) Staerk, H.; Mitzkuo, R.; Kühnle, W.; Weller, A. *Springer Ser. Chem. Phys.* **1982**, *23*, 205.  
(25) The difference between the behavior of radical ions generated from **2** and **3** is a subject of our current investigation.

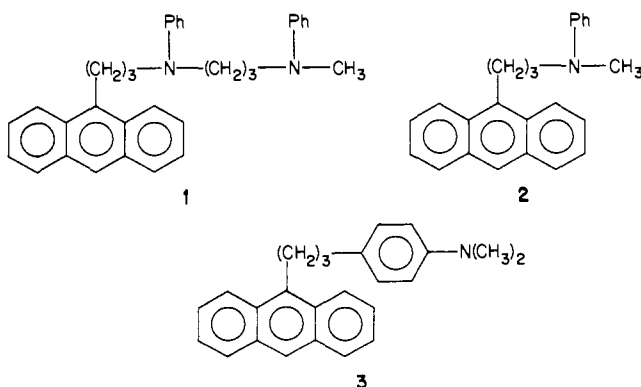
**Table I.** Excited State Behavior of 1-3

	1	2	3
In Dichloromethane			
fluorescence			
$\lambda_{\max}$	530 nm	530 nm	552 nm
$\phi_f^a$	<0.01	0.12	<i>b</i>
$\tau_f^a$	<2 ns <sup>c</sup>	28 ± 1 ns	<i>b</i>
absorption			
470 nm, $\tau_{\text{decay}}^d$	19 ± 3 ns	<i>e</i>	<i>b</i>
700 nm, $\tau_{\text{decay}}^{a,d,f}$	20 ± 1 ns	28 ± 2 ns	<i>b</i>
425 nm, $\tau_{\text{rise}}^{a,f}$	21 ± 2 ns	27 ± 2 ns	<i>b</i>
In Acetonitrile			
absorption			
470 nm, $\tau_{\text{decay}}^g$	2.0 ± 0.2 ns	2.0 ± 0.3 ns	270 ± 30 ps
700 nm, $\tau_{\text{decay}}^{f,g}$	2.0 ± 0.3 ns	1.6 ± 0.4 ns	270 ± 30 ps
425 nm, $\tau_{\text{rise}}^{f,g}$	1.8 ± 0.3 ns	2.5 ± 0.4 ns	<i>e</i>

<sup>a</sup>In deaerated solution. <sup>b</sup>Not measured. <sup>c</sup>Calculated from the quantum yield and the radiative lifetime of 1. <sup>d</sup>Rise time is <2 ns or instrument limiting. <sup>e</sup>No appreciable absorption detected with our instruments. <sup>f</sup>The values were the same within experimental error when they were measured over a 10-nm range. <sup>g</sup>Rise time is 10 ps or less, see also ref 19-21.

530 nm,  $\phi_f < 0.01$ ) in dichloromethane but yields the absorptions of both the dialkylanilino radical cation and the anthryl radical anion. Furthermore, in contrast to radical ions generated from photoexcited 1-3 in acetonitrile, the radical ions generated from 1 in dichloromethane exhibit a lifetime of 20 ± 3 ns, 10-75 times longer than those generated from 1-3 in acetonitrile, and annihilate to give anthryl triplet among the products (risetime, 21 ± 1 ns). All these times are about an order of magnitude longer than the estimated lifetime of the intramolecular exciplex form 1.

[Arene\*-dialkylaniline] exciplexes are highly polar systems which exhibit a dipole moment of approximately 10-13 D;<sup>16,26</sup> therefore, the exciplex exhibits a high effective polarity in its vicinity even in a nonpolar solvent. Since a photoexcited molecule is known to react with a donor to generate an ion pair in a polar environment, it is not surprising that a donor molecule will react with an exciplex in a nonpolar medium in view of this high effective polarity, while an excited "nonpolar" uncomplexed aromatic hydrocarbon cannot. The ion pair generated from 1 in this interaction differs from the intimate ion pairs generated from 2 and 3 in that the average distance between the donor and the acceptor is increased which may retard the back electron transfer (reaction 4). A similar suggestion has been made by Mataga and his



co-workers independently on a linked polychromophoric system containing one porphyrin group as the photoexcited donor and two quinoid groups as the acceptor.<sup>8,27</sup> Since amine dimer cation radicals have been implicated as intermediates in the exciplex quenching processes,<sup>8,28</sup> the anilino intermediate detected in our

(26) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183.

(27) The porphyrin-quinone systems differ from our arene-amine systems in that they form ground-state complexes and undergo light-induced electron transfer in nonpolar media,<sup>5</sup> while arene-amine systems do not.<sup>8</sup> However, the lifetime of ion pairs generated from the trichromophoric porphyrin-quinone system was increased over the bichromophoric one in dioxane from 140 to 300 ps.<sup>5</sup>

study may be such a species. The longer lifetime of ion pairs formed from excited 1 in dichloromethane may also be caused by the delocalization of the charge between the two anilino groups.

In conclusion, our investigation of the photochemical behavior of polychromophoric systems containing an anthryl group and one or two dialkylanilino groups demonstrates that the presence of the second anilino group promotes the electron transfer of arene-amine exciplexes to generate radical ion pairs in dichloromethane. These ion pairs exhibit an appreciably longer lifetime than the ion pairs generated from the electron transfer of photoexcited bichromophoric analogue in polar media. The results will assist us in the construction of other systems which may yield radical ions of even longer lifetimes. Such an investigation may lead to a better understanding of the conversion of light energy into chemical energy via electron transfer among organic compounds.

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(28) (a) Alder, R. W.; Sessions, R. B. In "The Chemistry of Amines, Nitroso, and Nitro Compounds"; Patai, S., Eds.: Wiley: New York, 1982; Chapter 18, p 763. (b) Nelsen, S. F.; Gannett, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 4698.

## Thermal Behavior of C<sub>8</sub>H<sub>8</sub> Hydrocarbons.<sup>1</sup> 2. Semibullvalene:<sup>2</sup> Kinetic and Thermodynamic Stability

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Semibullvalene SBV, (1) is a hydrocarbon, discovered by Zimmerman and Grunewald,<sup>3a</sup> remarkable for undergoing a rapid degenerate Cope rearrangement at -150 °C.<sup>3b,c</sup> We were led to investigate its higher temperature thermal behavior in connection with separate studies of the isomeric molecules, cyclooctatetraene (COT, 2)<sup>4</sup> and cubane.<sup>5</sup> There are conflicting reports of the product of SBV (1) decomposition. Two studies<sup>6,7</sup> claim COT (2) as the product while a third states that it reacts reversibly to

(1) Part 1: Martin, H.-D.; Urbanek, T.; Braun, R.; Walsh, R. *Int. J. Chem. Kinet.* **1984**, *16*, 117. This is also part 51 of "Small and Medium Rings" (Part 50: Honegger, E.; Heilbronner, E.; Urbanek, T.; Martin, H.-D. *Helv. Chim. Acta* **1985**, *68*, 23).

(2) Systematic name: tricyclo[3.3.0.0.2]octa-3,6-diene.

(3) (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. (b) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* **1974**, *96*, 2887. (c) For a general review of the thermal behavior of SBV (1), see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; p 232.

(4) Martin, H.-D.; Urbanek, T.; Walsh, R., unpublished results.

(5) Martin, H.-D.; Urbanek, T.; Pfohler, P.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1985**, 964.

(6) Paquette, L. A.; Russell, R. K.; Wingard, R. E., Jr. *Tetrahedron Lett.* **1973**, 1713.

(7) Stapersma, J.; Rood, I. D. C.; Klumpp, G. W. *Tetrahedron* **1982**, *38*, 2201.