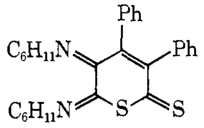
(13% yield), the structure illustrated was assigned to complex **6**.

In attempts to release the heterocyclic rings from these metallo-rings, we found that complex **3a** reacts with sulfur in benzene at 70° to afford 4,5-diphenyl 1,2-dithia-4-cyclopentene-3-thione, mp 160° (lit.[10] 159.5°), in almost quantitative yield. Cyclohexyl isocyanide also reacts with **3a** in a similar condition to give a 21% yield of pale yellow crystals (**7**) of the formula $C_{29}H_{32}N_2S_2$, mp 203°, mol wt 472 (mass spectrum), 472.7 (calcd). The structure of this compound may be written as shown below.



7

More extensive study on this type of reaction is in progress.

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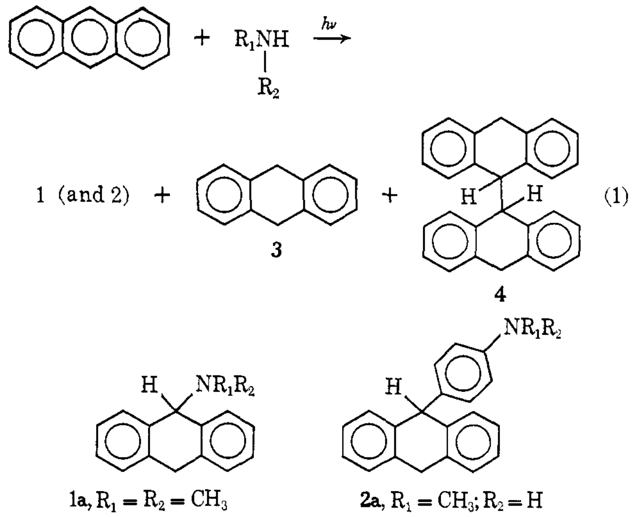
Chemistry of Exciplexes, Photochemical Addition of Secondary Amines to Anthracene

Sir:

Weller and his associates demonstrated that photoexcited arenes form exciplexes with tertiary amines which exhibit exciplex emission in nonpolar solvents.[1] Their contributions stimulated extensive investigations in this area.[2–7] In connection with their studies on arene–tertiary amine exciplexes, Mataga[2] and Nakajima[3] reported that secondary amines also quench the fluorescence of arenes but no exciplex emission was observed. This marked difference between the behaviors of these two groups of amines was, however, not understood. In this communication we wish to report that anthracene undergoes facile photochemical reactions with secondary amines in benzene and in acetonitrile. Mechanistic investigations suggested that these reactions proceed *via* exciplexes as intermediates and an important step in the decay of these exciplexes may involve the proton transfer from the secondary amine to the arene.



$1a, R_1 = R_2 = CH_3$
$b, R_1 = R_2 = C_2H_5$
$c, R_1 = C_6H_4; R_2 = CH_3$

$2a, R_1 = CH_3; R_2 = H$
$b, R_1 = R_2 = CH_3$

Irradiation of a solution of anthracene (0.01–0.05 *M*) and dimethylamine, diethylamine, or *N*-methylaniline (1.0 *M*) in benzene or in acetonitrile yielded both the 1:1 adduct(s) and the reduction products of anthracene (reaction 1). The 1:1 adduct was the 9-amino-9,10-dihydroanthracene (**1a–c**), respectively, but **1c** was accompanied with minor amounts of 9-(*p*-methylaminophenyl)-9,10-dihydroanthracene (**2a**). The reaction may thus be applied for the amination of anthracene at the meso position. Irradiation of anthracene with diethylamine-*d* resulted in the formation of photoproducts **1b**, **3**, and **4** containing deuterium at the meso positions. This observation suggests that proton transfer from the amine to anthracene may be involved in the formation of these products. On the other hand, irradiation of anthracene and *N*,*N*-dimethylaniline in benzene yielded exclusively the photodimer of anthracene but in acetonitrile it yielded a mixture of **2b**, **3**, and **4**.[8] We found that different amines quench the fluorescence of anthracene with different quenching efficiencies and that the quenching efficiencies are solvent dependent (Table I), amines with lower ionization potentials are more efficient quenchers and the quenching efficiencies are higher in acetonitrile than in benzene. We also observed that quantum yields of the consumption of anthracene in the presence of amines

Table I. Quenching of Anthracene Fluorescence by Amines[a]

Amine	IP, eV	Solvent	$k_q\tau$, mol^{-1} l.	C_h, *M*[b]
C_6H_5N-$(C_2H_5)_2$	7.15[c]	CH_3CN	91.0, 88.2[d]	0.011 ± 0.0005
		C_6H_6	39.0	0.026 ± 0.0005
C_6H_5-$NHCH_3$	7.34[c]	CH_3CN	78.5	0.0125 ± 0.0005
		C_6H_6	22.3	0.0448 ± 0.0005
$(C_2H_5)_2NH$	8.44[c]	CH_3CN	14.0	0.072 ± 0.002
		C_6H_6	3.1	0.324 ± 0.010
$(C_2H_5)_2ND$[e]		CH_3CN	12.2	0.082 ± 0.002
		C_6H_6	2.8	0.358 ± 0.010

[a] Anthracene concentration, 5 × 10^{-4} *M*; excitation at 350 nm. [b] Half-quenching concentrations. [c] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," E. Arnold, London, 1966. [d] A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968). [e] Isotopic purity, 80%.

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vary with both the nature of the amine and the solvent polarity (Table II); the tertiary amine reacts with photoexcited anthracene with higher quantum yield in acetonitrile than in benzene while secondary amines react with photoexcited anthracene with higher quantum yields in benzene than in acetonitrile. The results indicate that *the quenching of anthracene fluorescence by secondary and by tertiary amines proceeds via the same mechanism, while the photochemical reactions of anthracene with secondary amines proceed via a different mechanism from that with the tertiary amine.*

Table II. Quantum Yields for the Consumption of Anthracene in the Presence of Amines[a]

Amine	Solvent	% adducts 1	2	% reduction products 3	4	$\phi_{\text{-anth}}$[b]
$C_6H_5N(CH_3)_2$	CH_3CN[c]		60–65	5–10	10–20	0.58 ± 0.08
	C_6H_6[c,d]					0.14 ± 0.01
$C_6H_5NHCH_3$	CH_3CN[e]	59	5	Trace	Trace	0.19 ± 0.01
	C_6H_6[e,f]	35	18	Trace	9	0.56 ± 0.03
$(C_2H_5)_2NH$	CH_3CN[g]	28		18	19	0.19 ± 0.01
	C_6H_6[g]	43		22	19	0.48 ± 0.02
$(C_2H_5)_2ND$[h]	CH_3CN					0.19 ± 0.01
	C_6H_6[g]	39		20	25	0.43 ± 0.02
$(CH_3)_2NH$	C_6H_6[g]	54[i]		10	15	

[a] Anthracene concentration, 0.01 *M;* amine concentration, 1.0 *M;* all products have been characterized by elemental and spectral analyses; yields given are isolated yields. [b] Excitation at 365 nm. [c] Reference 8. [d] Photodimer of anthracene was the only product detected. [e] Preparative irradiation with an uranyl glass filter sleeve. [f] 1,2-Diphenyl-1,2-dimethylhydrazine was also isolated in 14% yield. [g] Preparative irradiation with a Pyrex glass filter sleeve. [h] Isotopic purity, 85%. [i] G. Wittig, G. Closs, and F. Mindesmann, *Justus Liebigs Ann. Chem.*, **594**, 89 (1955).

Since the quenching of excited anthracene by tertiary amines in nonpolar solvents proceeds *via* exciplexes, the qualitative correlation of ionization potentials of amines with their quenching efficiencies suggests that exciplexes may also be the intermediate in the quenching of excited anthracene by secondary amines.[9,10] The arene–amine exciplexes are known to possess appreciable charge transfer character and are more polar than the uncomplexed excited arenes;[11] consequently, their formation will be favored in polar solvents. The observed higher quenching efficiencies of secondary amines in a more polar solvent provide additional support for the role of exciplex in the quenching.

The amine concentrations used in the quantum yield determinations were much higher than the corresponding half-quenching concentrations (C_h's), and most excited anthracene existed as the corresponding exciplex. The quantum yield of anthracene consumption thus measures the portion of the exciplex which decays to give chemical products. In polar solvents like acetonitrile, the arene–tertiary amine exciplexes are known to undergo rapid electron transfer to give solvent separated ion pairs which subsequently give rise to products (reaction 2).[5-8] It is thus probable

$$\text{ArH*} + \text{amines} \longrightarrow [\text{ArH}\cdot^{-}\text{:amine}\cdot^{+}]^{*} \xrightarrow{\text{acetonitrile}} \text{ArH}\cdot^{-} + \text{amine}\cdot^{+} \quad (2)$$

that secondary amines also will undergo the electron transfer in acetonitrile. In nonpolar solvents like benzene, the electron transfer in the exciplex to give a more polar ion pair will be unfavorable. The anthracene–tertiary amine exciplexes may decay *via* exciplex fluorescence at low concentration of anthracene (5×10^{-4} *M*), but may react with another molecule of anthracene to give the photodimer at high concentration of anthracene (0.01 *M*). However, in the anthracene–secondary amine exciplexes the proton of the secondary amine may be transferred to the excited anthracene to give a radical pair (reaction 3) which may subsequently

$$\text{ArH*} + R_2NH \longrightarrow [\text{ArH}\cdot^{-}\text{:}R_2NH\cdot^{+}]^{*} \xrightarrow{\text{benzene}} \text{ArH}_2\cdot + R_2N\cdot \quad (3)$$

collapse to give the products. Since such a reaction will involve the formation of a homopolar intermediate from a more polar precursor, the transition will be favored in a nonpolar medium like benzene. The higher quantum efficiency of the anthracene–secondary amine reactions in benzene is compatible with such a process, and an analogus solvent effect in the photochemical intramolecular proton-transfer has been noted by Weller and his coworkers.[12]

Additional evidence to support the proton transfer as an important step in the decay of arene–secondary amine exciplex was obtained by studying the deuterium isotope effect. We found that the deuteration of diethylamine had no measurable effect on the quantum yield of the anthracene–diethylamine reaction in acetonitrile, but lowered the quantum yield in benzene.[13,14] Since the rate-determining step in the decay of exciplexes in acetonitrile is likely to involve the electron transfer from the amine to the excited hydrocarbon to give the ion pair, deuteration of the amino hydrogen will have little effect on the rate-determining step. On the other hand, the deuterium isotope effect in benzene verifies that the proton transfer from the secondary amine to the excited hydrocarbon is involved in the rate-determining step of the decay of the exciplex in nonpolar solvents.

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(14) Since this proton transfer is an intramolecular process with a nonlinear configuration and favorable energetics, it is not surprising that the magnitude of isotope effect is small, $k_h/k_d = 1.12$. See R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970); F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); J. L. Haslam, E. M. Eyring, W. W. Epstein, R. P. Jensen, and C. W. Jaget, *J. Amer. Chem. Soc.*, 87, 4247 (1965). The authors wish to thank Professors E. R. Thornton and L. Kaplan for some valuable discussions.