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Photochemical Reactions of Arenecarbonitriles with Aliphatic Amines. 1. Effect of Arene Structure on Aminyl vs. α-Aminoalkyl Radical Formation

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Abstract: The photochemical reactions of several singlet arenecarbonitriles with aliphatic amines have been investigated. The reactions of 9-phenanthrenecarbonitrile with diethylamaine and its N- and α-C-deuterated derivatives result in exclusive N–H atom transfer to yield the diethylaminyl and 9-cyano-9,10-dihydrophenanthren-9-yl radicals in benzene solution. Increased solvent polarity results in the formation of both diethylaminyl and 1-(ethylamino)ethyl radical. Similar results are obtained with 9-anthracenecarbonitrile. The competition between aminyl vs. α-aminoalkyl radical formation in this and other reactions is reviewed. Aminyl radical formation is characteristic of relatively nonpolar heteroexcimers in which hydrogen bonding may favor N–H transfer. Pure charge-transfer exciplexes, like alkoxyl radicals, yield predominantly the thermodynamically more stable α-aminoalkyl radical. The dominant reaction of the aminyl–phenanthren-9-yl radical pair in nonpolar solvent is combination to yield arene–amine adducts, which quantitatively lose HCN upon heating or chromatography. In contrast, the α-amino-alkyl–phenanthren-9-yl radical pairs formed in polar solvent disproportionate to yield reduced arene and oxidized amine, plausibly via radical pair electron transfer followed by proton transfer.

Introduction

The interaction of electronically excited organic molecules with tertiary amines has been extensively investigated and provides much of the basis for the present understanding of exciplex and radical ion pair phenomena.[1-3] The observation of exciplex fluorescence from numerous arene–amine exciplexes has allowed detailed spectroscopic investigations of these species. Addition of the α-C–H bond of trialkylamines to some arenes is attributed to an electron-transfer, proton-transfer mechanism (Scheme I).[3-7] Recent investigations of the mechanism of reactions of triplet benzophenone[8] and singlet *trans*-stilbene[7c] with trialkylamines indicate that proton transfer occurs via an exciplex (contact radical ion pair) intermediate and not a solvent-separated radical ion pair, confirming an earlier proposal by Bryce-Smith and Gilbert.[4b]

The interaction of singlet arenes with secondary amines results in the formation of short-lived, nonfluorescent exciplexes. Picosecond laser spectroscopic investigations of pyrene–secondary amine exciplexes indicate that the amine N–H group is hydrogen bonded to the pyrene π-orbitals in nonpolar solvent and that intersystem crossing is much more rapid than in the case of pyrene–tertiary amine exciplexes.[9] Chemical reactions of arene–secondary amine exciplexes normally result in 1,2- or 1,4-addition of the amine N–H bond to the arene or arene reduction via a mechanism analogous to that proposed for tertiary amines.[3,4b,7a,10] Addition of the α-C–H bond of secondary or primary amines to arenes is less common, having been reported only for reactions of benzenedicarbonitriles,[6] pyridine,[4c] and 1-phenylcyclohexene.[4d]

Scheme I. Mechanism of Addition of Benzene and Triethylamine[4a]

$$^1C_6H_6^* + Et_3N \longrightarrow {}^1(C_6H_6^{-\cdot} + Et_3N^{+\cdot})^* \longrightarrow (C_6H_7\cdot + Et_2N\dot{C}HCH_3) \longrightarrow$$

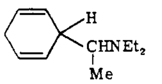

Table I. Kinetic Data for the Reaction of 9-Phenanthrenecarbonitrile and 9-Anthracenecarbonitrile with Diethylamine

arene	amine	solvent	$k_{qs}\tau_s$,[a] M^{-1}	$10^{-9}k_{qs}$,[b] $M^{-1}\,s^{-1}$
9-PCN	Et_2NH	C_6H_6	119 (103;[c] 85[d])	7.9
9-PCN	Et_2NH	CH_3CN	205 (238[c])	8.5
9-PCN	Et_2ND	C_6H_6	107	7.1
9-PCN	Et_2ND	CH_3CN	201	8.4
9-PCN	$(CH_3CD_2)_2NH$	C_6H_6	106	7.1
9-PCN	$(CH_3CD_2)_2NH$	CH_3CN	168	7.0
9-ACN	Et_2NH	C_6H_6	188	11.0

[a] Least-squares slopes of fluorescence-quenching Stern–Volmer plots, except as noted. [b] Calculated from Stern–Volmer slope and measured singlet lifetimes.[18] [c] Intercept slope ratio from Figure 1 for formation of I. [d] Intercept slope ratio from Figure 1 for formation of III.

The observation of both N–H and α-C–H addition of secondary amines to excited arenes suggests that either dialkylaminyl or α-aminoalkyl radical formation can occur, depending upon the reaction conditions (eq 1). Detailed investigations of the pho-

$$R_2CHNHR' \xrightarrow{-H\cdot} R_2CH\dot{N}R' \text{ or } R_2\dot{C}NHR' \qquad (1)$$

toreduction of benzophenone by secondary and primary amines by Cohen and co-workers[11] indicate that both N–H and α-C–H

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Table II, Quantum Yields for Product Formation from 9-Phenanthrenecarbonitrile and Diethylamine in Various Solvents[a]

solvent	e^b	n^c	Φ_I	Φ_{IIIa}
pentane	1.84	0.240	0.0030	0.033
cyclooctane	2.12	2.12	0,0032	0.049
benzene	2.28	0.645	0.0032(0.005)[d]	0.026(0.029)[d]
diethyl ether	4.34	0.242	0.0018	0.0082
ethyl acetate	6.02	0.455	0.00094	0.0016
tetrahydrofuran	7.58	0.55	0,0013	0.00079
acetonitrile	38.8	0.345	0.0031(0.003)[d]	*e*
sulfolane	43.3	10.29	0.0013	*e*
pentane–ethyl acetate 4:1	2.34		0.0025	0.024
pentane–ethyl acetate 3:2	2.84		0.0026	0.019
pentane–ethyl acetate 2:3	3.34		0.0029	0.018
pentane–ethyl acetate 1:4	3.84		0,0021	0.012
ethyl acetate–acetonitrile 4:1	12.6		0.0012	0.00056
ethyl acetate–acetonitrile 3:2	19.2		0.0017	0.00034
ethyl acetate–acetonitrile 2:3	25.7		0,0021	0.00016
ethyl acetate–acetonitrile 1:4	32.2		0.0030	*e*

[a] Values for deoxygenated solutions of 9-PCN (0.01 M) and diethylamine (0.12 M). Limits of error for relative values are small (<20%). Limits of error for absolute values increase with decreasing quantum yield (e.g., 0.01 ± 0.003, 0.001 ± 0.001). [b] Solvent dielectric constants for pure solvents from ref 19. Values for mixed solvents calculated assuming $e = \Sigma_i e_i V_i$, where V_i is the volume fraction of component i. [c] Solvent viscosities (cp) from ref 19. [d] Values from intercepts of Figure 1. [e] Value too small to measure,

atom abstraction can occur but that the latter process is apparently favored, α-Aminoalkyl–benzophenone ketyl radical pairs proceed to products efficiently, whereas aminyl–benzophenone ketyl radical pairs disproportionate to yield starting materials. Similarly, pulsed radiolysis of primary and secondary amines is proposed to yield both α-aminoalkyl and aminyl radicals; however, product formation is predominantly from α-aminoalkyl radicals.[12] While there have been conflicting reports concerning the relative yields of α-aminoalkyl vs. aminyl radical formation from reactions of *tert*-butoxyl radicals with amines,[13] the most recent kinetic data suggests that $k_{C-H}/k_{N-H} \geqslant 5$ for several primary and secondary amines.[14] While this result is in accord with the most recently estimated bond dissociation energies, $DH°$ (Me_2N–H) = 96 kcal/mol[15] and $DH°$ ($MeNHCH_2$–H) = 87 kcal/mol,[16] it does not account for the frequent observation of aminyl radical formation from amines in photochemical and pulse radiolysis reactions.

We report here the results of our investigations of the reactions of singlet 9-phenanthrenecarbonitrile (9-PCN), 9-anthracenecarbonitrile (9-ACN), and α-phenylcinnamonitrile (α-CCN) with diethylamine in nonpolar and polar solvents.[17] Analysis of reduction and addition products obtained using both N- and α-C-deuterated amines establishes that N-H abstraction is the predominant mode of reaction in nonpolar solvent but that increased solvent polarity leads to significant competing α-C-H abstraction. These results serve to further elucidate the mechanism of formation and the chemical behavior of α-aminoalkyl and aminyl radicals.

Results

Fluorescence Quenching, The fluorescence of 9-PCN and 9-ACN is quenched by diethylamine and its N- and α-deuterated derivatives. Values of $k_{qs}\tau_s$ obtained from the least-squares slopes of fluorescence-quenching Stern–Volmer plots in deoxygenated benzene or acetonitrile solution are given in Table I. The fluorescence-quenching rate constants (k_{qs}) are calculated using the reported singlet lifetimes for 9-PCN and 9-ACN.[18] Values of k_{qs} approach the rate of diffusion in benzene (1.6×10^{10} M^{-1} s^{-1}) and acetonitrile (2.9×10^{10} M^{-1} s^{-1}) solution.[19] The variations in k_{qs} with amine deuteration are within the limits of experimental error (±10%). The singlet state of α-CCN is nonfluorescent at room temperature in solution.[20] No exciplex emission is observed to accompany fluorescence quenching.

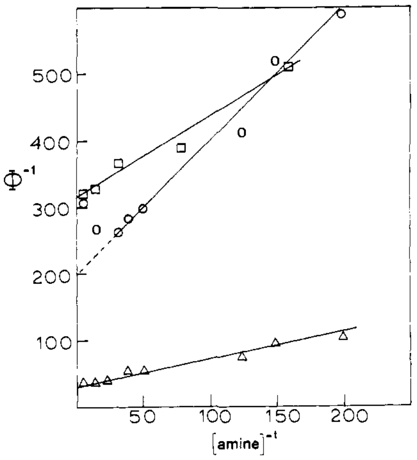
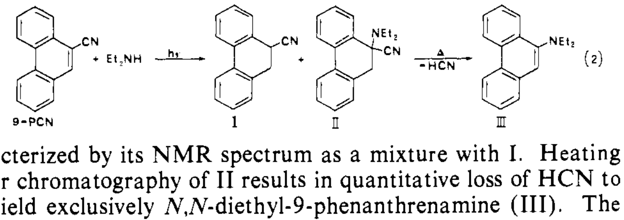


Figure 1, Amine concentration dependence of the quantum yield for the formation of reduction product I in benzene (○) and acetonitrile (□) solution and of substitution product III (△) from the reaction of 9-phenanthrenecarbonitrile and diethylamine in benzene solution.

Reaction of 9-Phenanthrenecarbonitrile with Diethylamine, Irradiation of 9-PCN (0.016 M) and diethylamine (0.11 M) in nitrogen-purged benzene solution with a Pyrex-filtered mercury lamp results in essentially quantitative conversion of 9-PCN to a mixture (ca. 1:8) of 9,10-dihydrophenanthrene-9-carbonitrile (I) and 9-(diethylamino)-9,10-dihydrophenanthrene-9-carbonitrile (II) (eq 2). Adduct II cannot be isolated but is readily characterized by its NMR spectrum as a mixture with I. Heating or chromatography of II results in quantitative loss of HCN to yield exclusively *N*,*N*-diethyl-9-phenanthrenamine (III). The spectral properties of I and III are identical with those of inde-



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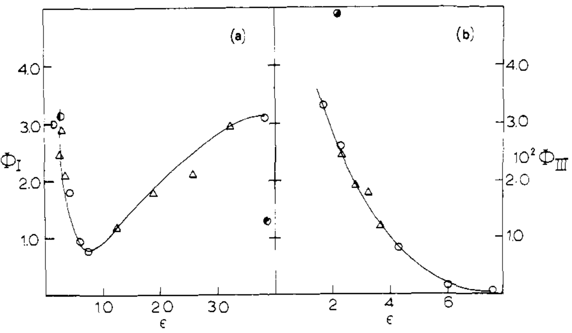


Figure 2. Effect of solvent polarity on the quantum yield for formation of (a) reduction product I and (b) substitution product III in pure (○) and mixed (△) solvents (◐ = sulfolane, ◑ = cyclooctane).

pendently synthesized samples. The only other product of the preparative irradiation detected by NMR or GC-MS analysis is *N*-ethylideneethylamine. Tetraethylhydrazine could not be detected and was found to be relatively stable under the reaction conditions.

Quantum yields for the formation of products I and III are dependent upon amine concentration, solvent polarity, and solvent viscosity. Plots of Φ^{-1} vs. $[\text{amine}]^{-1}$ for product formation are shown in Figure 1. These plots are linear for [amine] < 0.05 M, in accord with standard singlet quenching kinetics (eq 3).

$$\Phi^{-1} = \Phi_{\text{lim}}^{-1}(1 + k_{qs}\tau_s[\text{amine}])^{-1} \qquad (3)$$

Values of the limiting quantum yields for product formation at infinite amine concentration (Φ_{lim}) and $k_{qs}\tau_s$ obtained from the intercept and intercept/slope ratios in Figure 1 are reported in Tables II and I, respectively. Given the substantial error in the absolute value of such small quantum yields (±25%), the agreement between the $k_{qs}\tau_s$ values obtained from product formation and fluorescence quenching is considered satisfactory and supports the assumption of a singlet state mechanism for the formation of both reduction (I) and substitution (III) products. For [amine] > 0.05 M plots of Φ^{-1} vs. [amine] in benzene solution display upward curvature which is more pronounced for the formation of I than III.

Quantum yields for product formation from singlet 9-PCN (0.01 M) in several pure and mixed solvents are given in Table II.[19] Values of Φ_I decrease with increasing solvent polarity in the range $\epsilon < 8$ but increase in more polar solvents. Values for pure and mixed solvents fit the same curve with the exception of the most viscous of the polar solvents, sulfolane (Figure 2a). Values of Φ_{III} decrease continuously with increasing solvent dielectric constant with the exception of the most viscous of the nonpolar solvents, cyclooctane (Figure 2b).

In order to obtain further information about the mechanism of the reaction of 9-PCN with diethylamine, the effects of amine deuteration were investigated using both Et_2ND and $(CH_3CD_2)_2NH$. The latter amine was conveniently prepared by the reduction of diacetamide with lithium tetradeuterioaluminate. Irradiation of 9-PCN and Et_2ND in benzene solution to ca. 95% conversion yields, by NMR analysis, adduct II with stereorandom incorporation of 1.0 deuterium atom at C-10. Chromatography of this adduct yields III with ca. 50% deuteration at C-10. In view of the known preference of 9,10-dihydrophenanthrenes for anti elimination,[21] this result is indicative of stereorandom addition of Et_2ND to singlet 9-PCN. Also obtained by chromatography of the reaction mixture were I with 108% and 42% (±10% error limit) deuteration at C-10 and C-9, respectively, and recovered 9-PCN with 30% deuteration at C-10. Since deuteration of 9-PCN might affect the observed extent of deuterium incorporation in products I and II, the extent of deuteration of 9-PCN was determined as a function of conversion by mass spectral analysis. The resulting plot of % d_1 vs. conversion displays upward curvature (Figure 3). The value at 50% conversion (ca. 7% d_1) represents the approximate extent of deuterium incorporation in products I and II which can be derived from deuterated 9-PCN. Since this value is within the error limits of our measurements, no correction of the experimental data for I and II has been made.

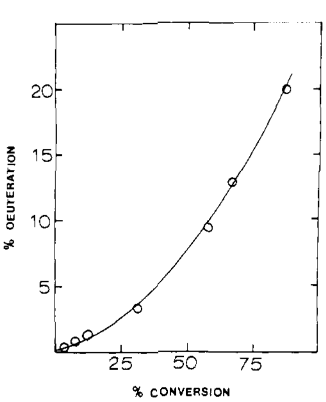


Figure 3. Incorporation of deuterium from diethylamine-*N*-*d* at C-10 of 9-phenanthrenecarbonitrile as a function of conversion.

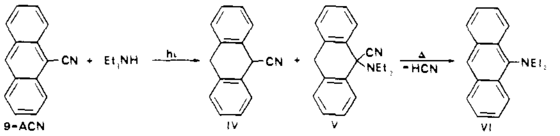
Table III. Quantum Yields for Product Formation from 9-Phenanthrenecarbonitrile and Deuterated Diethylamines[a] and Deuterium-Labeling Results

amine	solvent	Φ_I[a]	Φ_H/Φ_D	% D-10[b]	% D-9[b]	Φ_{III}[a]	Φ_H/Φ_D
Et_2NH	C_6H_6	0.0032				0.026	
Et_2ND	C_6H_6	0.0019	1.7	108	42	0.015	1.7
$(CH_3CD_2)_2NH$	C_6H_6	0.0028	1.1	11	45	0.027	0.95
Et_2NH	CH_3CN	0.0030					
Et_2ND	CH_3CN	0.0030	1.0	52	25		
$(CH_3CD_2)_2NH$	CH_3CN	0.0032	0.94	30	38		

[a] See Table II, footnote *a*. [b] Deuterium content in I determined by by ^1H NMR peak integration compared to undeuterated samples (±10%).

Markedly different results are obtained upon irradiation of 9-PCN and $(CH_3CD_2)_2NH$ in benzene solution. No deuterium incorporation at C-10 is detected (<10%) in either the substitution product III or recovered 9-PCN. Reduction product I contains 0.11 and 0.45 equiv of deuterium at C-10 and C-9, respectively. Irradiation of 9-PCN and Et_2ND in acetonitrile solution results in the formation of I with 52% and 25% deuteration at C-10 and C-9, respectively, and no detectable deuteration of recovered 9-PCN. Irradiation of 9-PCN and $(CH_3CD_2)_2NH$ in acetonitrile solution results in the formation of I with 30% and 38% deuteration at C-10 and C-9, respectively, and no detectable deuteration of recovered 9-PCN. Quantum yields for the formation of I and III with deuterated and undeuterated diethylamine are summarized in Table III along with deuterium labeling results for I. There is no appreciable effect of deuteration upon the quantum yields for product formation except in the reaction of 9-PCN with Et_2ND in benzene solution.

Reaction of 9-Anthracenecarbonitrile with Diethylamine. Irradiation of 9-ACN (0.033 M) and diethylamine (0.20 M) in benzene solution results in the formation of a mixture (ca. 1:10) of reduction product IV and adduct V. Heating or chromatography quantitatively converts V to *N*,*N*-diethyl-9-anthracenamine (VI, eq 4). Quantum yields for the formation of IV and VI are similar to those for the formation of I and III (Table II). Irradiation of 9-ACN and diethylamine in acetonitrile solution yields the [4 + 4] photodimer of 9-ACN as the major product.



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Irradiation of 9-ACN and Et_2ND in benzene solution results in the formation of adduct V with 100% C-10 deuteration. Based

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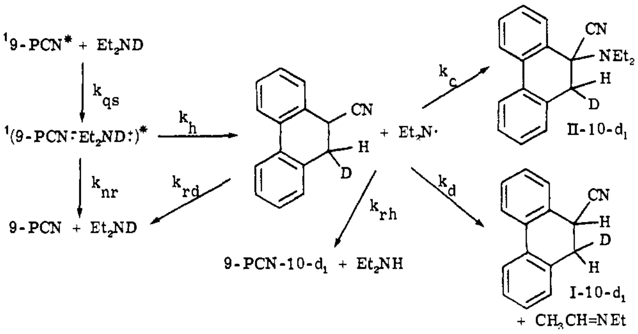
Table IV. Arene Energetics and Quantum Yields for Reaction with Diethylamine in Nonpolar Solvent

arene	E_S,[a] eV	$-E_A{}^{red}$[a,b] eV	E_{ex},[c] eV	E_T,[a] eV	Φ_{rdn}[d]	Φ_{add}[d]
benzene	4.76	2.40	3.73	3.31		+[i]
anthracene	3.27	1.96	3.29	1.82	0.20[j]	0.21[j]
trans-stilbene	3.53	2.26	3.59	2.12	0.06[k]	0.09[k]
benzonitrile	4.50	2.26[f]	3.59	3.05		+[l]
1-naphthonitrile	3.84	2.01	3.34	2.49		+[m]
9-phenanthrenecarbonitrile	3.42	1.91	3.24	2.54	0.003	0.03
9-anthracenecarbonitrile	3.04	1.50	2.83	1.82	0.005	0.02
α-phenylcinnamonitrile	3.53	1.58	2.91	2.0[h]	+	+
1,4-benzenedicarbonitrile	4.27	1.51[f]	2.84	3.03		+[n]
3,10-phenanthrenedicarbonitrile	3.38[e]	1.57[g]	2.90	2.51[e]	0	0
3,9-phenanthrenedicarbonitrile	3.33[e]	1.51[g]	2.84	2.42[e]	0	0

[a] Values from ref 19 except as noted. [b] Values from ref 20, except as noted, vs. SCE in nonaqueous dolution. [c] Calculated by using eq 6. [d] Values from this work or as noted. [e] Values from ref 18a. [f] Bartak, D.; Houser, K. J.; Rudy, B. C.; Hawley, M. D. *J. Am. Chem. Soc.* 1972, *94*, 7526-7430. [g] Park, S.-M.; Caldwell, R. A. *J. Electrochem. Soc.* 1977, *124*, 1859-1864. [h] Estimated values. [i] Reference 4b. [j] Values estimated from data in ref 10. [k] Reference 7a. [l] Reference 4c. [m] Reference 30. [n] Reaction in acetonitrile solution.[6]

Scheme II. Reaction of Singlet 9-Phenanthrenecarbonitrile with Et_2ND in Benzene Solution



on NMR integration, addition of Et_2ND is 67% syn and 33% anti. Chromatography of adduct V-*d* on silica gel yields VI with ca. 75% deuteration at C-10. This result is consistent with stepwise ionic 1,4-elimination, which is known to be selective for loss of a proton vs. deuteron.[22] Also formed in the reaction of 9-ACN and Et_2ND in benzene solution is reduction product IV with 100% deuteration at C-10 and 10% deuteration at C-9.

Reaction of (*Z*)-α-Phenylcinnamonitrile with Diethylamine. The reaction of α-CCN with diethylamine differs from that of 9-PCN and 9-ACN in that the reduction product VII is the only product detected in benzene or more polar solvents. The substitution product VIII can be detected as a minor product in pentane solution. Irradiation of α-CCN (0.03 M) and diethylamine (0.20 M) in pentane solution results in $Z \rightarrow E$ isomerization and the formation of 2,3-diphenylpropionitrile (VII) and *N*,*N*-diethyl-1,2-diphenylethenamine (VIII) in a ca. 10:1 ratio (eq 5). Also

$$\underset{\alpha\text{-CCN}}{PhCH{=}C(CN)Ph} + Et_2NH \xrightarrow[C_5H_{12}]{h\nu} \underset{VII}{PhCH_2CH(CN)Ph} + \underset{VIII}{PhCH{=}C(NEt_2)Ph} \quad (5)$$

formed are small amounts of the products observed upon irradiation of 9-PCN (eq 2), which is presumed to be formed via electrocyclic reaction of (*E*)-α-CCN. Irradiation of α-CCN and Et_2ND in benzene solution yields VII with no detectable deuterium incorporation (<10%) at C-3 and ca. 50% deuteration at C-2.

Discussion

A plausible mechanism for the reaction of singlet 9-PCN with Et_2ND in nonpolar solvent is shown in Scheme II. The formation of a nonfluorescent singlet exciplex or contact radical ion pair $^1(9\text{-PCN}^{-}\cdot Et_2NH^{+}\cdot)^*$ is consistent with previous observations of exciplex formation between arenes and secondary amines and the observation of k_{qs} values near the rate of diffusion (Table I).[1-3,9] Diffusion-controlled quenching is expected when the free energy of the exciplex (E_{ex}) is lower than that of the locally excited singlet state (E_s).[1] The approximate value of E_{ex} in nonpolar solvent can be calculated using Weller's equation (eq 6),[1] where $E_A{}^{red}$ is the

$$E_{ex} = E_D{}^{ox} - E_A{}^{red} + 0.32 \pm 0.1 \text{ eV} \qquad (6)$$

reduction potential of the arene and $E_D{}^{ox}$ is the reduction potential of the amine. Using values of $E_A{}^{red} = -1.91$ V[20] and $E_D{}^{ox} = 1.01$ V[23] (both vs. Ag/AgCl in acetonitrile solution), a value of $E_{ex} = 3.24$ eV is calculated for the 9-PCN–diethylamine exciplex. This value is less than the singlet energy of 9-PCN (3.42 eV), rendering exciplex formation exothermic by ca. 0.2 eV. Values of E_s and E_{ex} for several arenes and arene–diethylamine exciplexes are summarized in Table IV. The absence of a deuterium isotope effect on the fluorescence-quenching process is consistent with rate-determining exciplex formation.

According to Scheme II, the singlet exciplex can either undergo proton transfer to yield a radical pair (k_h) or decay to the ground state by nonradiative processes (k_{nr}). Intersystem crossing is reported to be substantially faster for pyrene–secondary amine vs. pyrene–tertiary amine exciplexes.[9] The formation of both reduction and addition products via a common singlet exciplex intermediate is supported by the observation of similar Stern–Volmer constants for fluorescence quenching and the formation of I and III (Figure 1).

The results of deuterium-labeling studies (Table III) indicate that N–H(D) transfer is the predominant process leading to the formation of both I and II in nonpolar solvent. The formation of both products via a common radical pair is consistent with the observation of quantitative C-10 deuteration of I and II using Et_2ND but not $(CH_3CD_2)_2NH$ and with the observation of product formation isotope effects using Et_2ND but not $(CH_3CD_2)_2NH$ (Table III). Formation of a radical pair intermediate is also consistent with the stereorandom formation of II-*10-d*, and the incorporation of deuterium into recovered 9-PCN. Disproportionation to yield 9-PCN-*10-d* and Et_2NH (k_{rh}) competes inefficiently with formation of I and II (Figure 3). Disproportionation to yield recovered starting materials (k_{rd}) should be slower than disproportionation with deuterium incorporation ($k_{rh} \geq k_{rd}$); however, reabstraction of deuterium prior to reorientation of the radical pair cannot be distinguished from other nonradiative decay pathways. The mechanism for hydrogen isotope exchange in 9-PCN is analogous to that previously postulated for tritiation of benzonitrile by Et_2NT.[24]

Radical pair disproportionation to yield I and *N*-ethylideneethylamine (Scheme I, k_d) should result in the formation of I with no deuterium incorporation at C-9 using Et_2ND and 100% deuterium incorporation at C-9 using $(CH_3CD_2)_2NH$. Since ca. 50% C-9 deuteration is observed with both amines, this pathway can account for no more than half of product I. Thus reactions of

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cage-escaped 9-cyano-9,10-dihydrophenanthren-9-yl radicals must account for $\geq 50\%$ of product I. In accord with a cage-escape pathway for the formation of I, increased solvent viscosity (Table III, compare benzene and cyclooctane) increases the quantum yield for the formation of III but not I. Several cage-escape processes can account for the observed extent of C-9 deuterium incorporation in I. Among these are (a) disproportionation of two phenanthren-9-yl radicals to yield I and 9-PCN, (b) abstraction of N–H from a second amine molecule by phenanthren-9-yl radical, and (c) abstraction of α-C–H from a second molecule of amine by the aminyl radical to yield an α-aminoalkyl radical (eq 7), which

$$\mathrm{Et_2N\cdot + Et_2NH \rightarrow Et_2NH + CH_3\dot{C}HNHEt} \qquad (7)$$

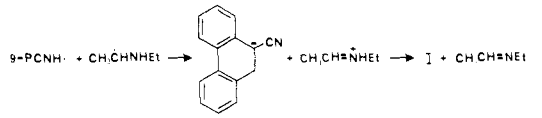
disproportionates with the phenanthren-9-yl radical. Paths a and b fail to account for the absence of tetraethylhydrazine, an expected product of diethylaminyl radical selftermination.[28] This observation, plus literature precedents for aminyl to α-aminoalkyl interconversion,[12,13] led us to support path c in a preliminary communication.[17] Nazran and Griller[14] have subsequently questioned the occurrence of reaction 7 on the basis of the predominant (90 ± 10%) second-order decay of diethylaminyl radicals generated by laser flash photolysis of tris(diethylamino)phosphine with di-*tert*-butyl peroxide in the presence of 1 M diethylamine. However, as they point out, first-order decay processes (eq 7) may compete more effectively with second-order decay at the low concentration of diethylaminyl radicals formed upon steady-state irradiation ($I \sim 2.5 \times 10^{-7}$ Einstein s^{-1}). While aminyl radicals are classified as "feeble dehydrogenating agents", they will abstract hydrogen from alkane solvents when selfreactions are hindered.[25] Thus we still favor path c as providing the most satisfactory explanation of the deuterium-labeling results as well as a possible explanation for the effect of high amine concentration upon product quantum yields (Figure 1). Occurrence of reaction 7 would lower the yield of II and might also lower the yield of I by favoring disproportionation to starting materials (Scheme II).

While deuterium-labeling studies indicate that reaction of singlet 9-PCN and diethylamine in benzene solution occurs via exclusive N–H transfer, such is not the case for reaction in acetonitrile solution. The observation of 52% C-10 deuteration of I with $\mathrm{Et_2ND}$ and 30% C-10 deuteration of I with $\mathrm{(CH_3CD_2)_2NH}$ indicates that N–H and α-C–H transfer are competitive processes. The absence of a significant isotope effect on product quantum yields with either amine (Table III) is also indicative of nonselective N–H vs. α-C–H abstraction. Solvent induced changes in bimolecular photochemical reactions have been attributed to the intermediacy of exciplexes in nonpolar solvents and radical ion pairs in polar solvents.[7b,10a] Recent investigations of the reactions of triplet benzophenone and singlet *trans*-stilbene with tertiary amines in polar solvents have established that proton transfer occurs via short-lived contact radical ion pairs (exciplexes) and not via longer-lived solvent-separated radical ion pairs.[7e,8] Since complete solvation of the amine cation radical should inhibit proton transfer to the anion radical, we assume that proton transfer occurs in all cases via an exciplex or contact radical ion pair.

If proton transfer occurs via an exciplex intermediate in both polar and nonpolar solvents, why are the competition between initial N–H vs. α-C–H transfer and the product quantum yields (Figure 2a,b) highly dependent upon solvent polarity? Increased solvent polarity can affect exciplex behavior both by changing the electronic structure and geometry of the exciplex and shortening its lifetime.[1,2] Using the standard resonance description of the exciplex as a hybrid of locally excited and charge transfer configurations (eq 8), the electronic structure of the 9-PCN–diethylamine exciplex may change from that of a heteroexcimer (a – b) in nonpolar solvent to that of a contact radical ion pair (a << b) in polar solvent. The more ionic contact radical ion pair should be more reactive and thus less selective toward N–H vs. α-C–H or H vs. D abstraction, as is observed. The geometry of the exciplex may also be altered by amine–solvent hydrogen bonding which could be disrupting the interaction of the N–H and arene observed in nonpolar solvent.[9] The greater basicity of ethyl acetate vs. pentane or acetonitrile thus could account for the minimum in Figure 2a. Polar solvents also accelerate formation of solvent separated radical ion pairs and other singlet exciplex nonradiative decay pathways, thus shortening the lifetime of the exciplex.[1,2] The minimum observed in Figure 2a may thus reflect a decrease in exciplex lifetime for solvents of $\epsilon < 8$ and an increase in exciplex reactivity in more polar solvents. The low quantum yield observed in the highly viscous polar solvent sulfolane (Table II) reflects incomplete quenching of singlet 9-PCN by 0.12 M diethylamine.

$$\psi(\mathrm{AD})^* = a\psi(\mathrm{A^*D}) + b\psi(\mathrm{A^{-}\cdot D^{+}\cdot}) \qquad (8)$$

Deuterium-labeling studies establish that both aminyl and α-aminoalkyl radicals are formed in acetonitrile solution; however, neither radical yields a combination product with the phenanthren-9-yl radical. The absence of radical combination products indicates that either radical disproportionation or cage escape must be more rapid than combination. Cage escape is dependent upon solvent viscosity, but not polarity.[26] Even in the highly viscous polar solvent sulfolane no radical pair combination is observed (Table III). Thus increased solvent polarity must favor radical pair disproportionation vs. combination. Furthermore, the absence of deuterium incorporation in recovered 9-PCN in acetonitrile solution indicates that radical pair disproportionation is selective for formation of products vs. starting materials (Scheme I, k_d vs. k_{rd}). While radical pair termination reactions are not normally sensitive to solvent polarity,[26] this generalization may not apply to the radical pairs of the present investigation. The phenanthren-9-yl radical has a very high electron affinity, as evidenced by the low oxidation potential (–0.1 V) of the carbanion generated by deprotonation of I.[27] Furthermore, α-aminoalkyl radicals are much more readily oxidized than their parent amines[23] and have the lowest ionization potentials of any reported organic species.[16] Thus the absence of phenanthren-9-yl–α-aminoalkyl radical coupling products may well be due to facile electron transfer followed by proton transfer (eq 9).[28] The formation of I via two sequential electron-transfer–proton-transfer reactions (Scheme I and eq 7) is analogous to the mechanism of electrochemical and alkali metal reduction of phenanthrenes.[27] The absence of phenanthren-9-yl–aminyl radical combination in acetonitrile solution might be due to an analogous radical pair electron-transfer–proton-transfer reaction; however, there is no apparent precedent for the oxidation of aminyl radicals to dialkylnitrogen cations.[25b]



(9)

Alternatively, occurrence of reaction 7 could yield the phenanthren-9-yl–α-aminoalkyl radical pair which would disproportionate via reaction 9. While it is not possible to rule out either alternative, the former appears to be more consistent with the low levels of C-9 deuteration of product I with $\mathrm{Et_2ND}$ (25%) and $\mathrm{(CH_3CD_2)_2NH}$ (38%) in acetonitrile solution and the absence of a pronounced solvent viscosity effect upon product formation in acetonitrile vs. sulfolane.

The reaction of 9-ACN with diethylamine in benzene solution (eq 4) evidently occurs via the formation of the 9-cyano-9,10-dihydroanthracen-9-yl–diethylaminyl radical pair. Deuterium-labeling studies support the occurrence of highly selective N–H vs. α-C–H proton transfer, as is observed in the reaction of 9-PCN with diethylamine. Subtle differences do occur in the behavior of the radical pairs formed from 9-ACN vs. 9-PCN. In the case

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of 9-PCN with Et_2ND, radical pair combination (Scheme II, k_c) is a stereorandom process, whereas in the case of 9-ACN the ratio of syn/anti addition is ca. 2/1. The slight preference for syn addition indicates that radical pair bonding is slightly faster than reorientation for 9-ACN but not for 9-PCN. The level of C-9 deuteration of reduction product IV from the reaction of 9-ACN and Et_2ND is lower than that in I (10% vs. 42%). Thus in-cage disproportionation (Scheme II, k_d) can account for most of the formation of IV, but not of V.

The reaction of α-CCN with diethylamine differs from those of 9-PCN and 9-ACN in that no addition of substitution product can be detected in benzene or more polar solvents. The substitution product VIII can only be detected as a minor product in pentane solution (eq 5). Furthermore the absence of deuterium incorporation at C-3 in the reduction product VII formed upon irradiation of α-CCN and Et_2ND in benzene solution indicates that photoreduction occurs via selective α-C–H transfer (eq 10).

$$\underset{\alpha\text{-CCN}}{\mathrm{PhCH{=}C(CN)Ph}} + \mathrm{Et_2ND} \xrightarrow{h\nu} \mathrm{PhCH_2\dot{C}(CN)Ph} + \mathrm{CH_3\dot{C}HNDEt} \rightarrow \underset{\mathrm{VII}}{\mathrm{PhCH_2CD(CN)Ph}} + \mathrm{CH_3CH{=}NEt} \quad (10)$$

In-cage disproportionation can account for the 50% C-2 deuteration of VII, while cage-escape pathways lead to undeuterated VII.

Concluding Remarks. Investigation of the photochemical reactions of singlet 9-PCN and 9-ACN with deuterated secondary amines establishes that N–H transfer to yield an aminyl radical is the predominant pathway leading to both reduction and addition products in nonpolar solvent (Scheme II). The observation of predominant N–H transfer in nonpolar solvent is consistent with several literature reports of amine N–H addition to singlet arenes (benzene,[4b] anthracene,[10] *trans*-stilbene[7]), benzonitrile,[29] and 1-naphthonitrile.[30] In contrast several arenedicarbonitriles fail to yield N–H adducts with secondary amines. The reaction of benzenedicarbonitriles with diethylamine in acetonitrile solution leads to inefficient substitution of the amine for one cyano group with bonding at the α-carbon.[6] Reaction of 9,10-anthracenedicarbonitrile with diethylamine in acetonitrile solution is reported to yield 10-amino-9-anthracenecarbonitrile via attack of the anion of 9,10-dihydro-9,10-anthracenedicarbonitrile on the solvent.[31] We find that irradiation of diethylamine with 3,9- or 3,10-phenanthrenedicarbonitrile in benzene solution fails to yield reaction products, even though the singlet arene is efficiently quenched by the amine.

The efficiency of amine N–H addition to singlet arenes is dependent upon solvent polarity as well as arene structure. The quantum yield for N–H addition of diethylamines to the arenecarbonitriles 9-PCN, 9-ACN, and α-CCN decreases precipitously with increasing solvent polarity (Figure 2b). A similar trend is observed in the photoreduction of 4-chlorobiphenyl by Et_2ND; the extent of deuterium incorporation into the product biphenyl decreases with increasing solvent polarity.[4f] The decrease in N–H addition efficiency is more gradual with singlet anthracene[10] or *trans*-stilbene.[7a] A likely explanation for these observations is found in the tabulation of arene singlet and triplet energies and exciplex energies given in Table IV. Energies for pure charge transfer exciplexes calculated using eq 6 are seen to be virtually the same as the singlet energies of anthracene and *trans*-stilbene. Thus these arenes may interact with diethylamine to form relatively nonpolar heteroexcimers, which are not highly sensitive to solvent polarity.[7b] The arenecarbonitriles 9-PCN and 9-ACN form more polar exciplexes as a consequence of moderately exothermic (ca. 0.2 eV) electron transfer and these exciplexes are highly sensitive to solvent polarity. Finally, electron transfer from diethylamine to singlet α-CCN and the phenanthrenedicarbonitriles is highly exothermic (≥0.4 eV) leading to the formation of pure charge-transfer exciplexes even in benzene solution.[8] These exciplexes fail to react via N–H abstraction even in nonpolar solvents. The nonreactivity of the phenanthrenedicarbonitrile–amine exciplexes may also reflect the low E_{ex}–E_T energy gaps, which should result in rapid exciplex intersystem crossing.[9,32]

Transfer of the N–H diethylamine appears to be a process that is observed only for relatively nonpolar, singlet heteroexcimers. The more polar singlet arene–amine exciplexes, like the triplet benzophenone–amine exciplexes,[11] selectively transfer the amine α-C–H. Selective formation of the more stable α-aminoalkyl radical is also observed in the reactions of primary and secondary amines with *tert*-butoxyl radicals.[14] What then is unique about arene–amine heteroexcimers that leads to aminyl radical formation? A plausible explanation is provided by the proposal of Okada, Karaki, and Mataga[9] that singlet pyrene forms a heteroexcimer with primary or secondary amines in nonpolar solvent in which the amine N–H forms a hydrogen bond to pyrene. Such a geometry might indeed favor N–H vs. α-C–H transfer. If this N–H arene interaction is not present in pure charge-transfer exciplexes and triplet exciplexes, the absence of N–H transfer in these complexes can be readily rationalized.

Experimental Section

General. Melting points were determined by using a Fisher-Johns melting point apparatus and are uncorrected. Ultraviolet absorption spectra were measured by using a GCA/McPhearson EU-700 spectrophotometer. Fluorescence spectra were obtained by using a Perkin-Elmer MPF-44A fluorescence spectrometer and are corrected. Infrared spectra were obtained on a Perkin-Elmer 283 infrared spectrometer. NMR spectra were recorded on a Varian EM-360, Varian CFT-20, or JEOL FX-90Q spectrometer. Mass spectra were obtained on a Hewlett-Packard 5985 GC mass spectrometer system with a HP-5840A gas chromatograph.

The light source for all experiments was a 450-W Hanovia medium-pressure mercury-vapor lamp enclosed in a water-cooled Pyrex-glass well. The 313-nm mercury line was isolated by a potassium chromate filter when necessary. Quantum yields were measured using a Rayonet merry-go-round immersed in a water bath. Quantum yields were measured using 0.01 M arene carbonitrile and 0.12 M diethylamine in 13-mm o.d. Pyrex-glass tubes purged with nitrogen.

Fluorescence quenching studies were performed on 3-mL samples of 9-PCN or 9-ACN ($\sim 5 \times 10^{-5}$ M) in 13-mm o.d. Pyrex tubes purged with nitrogen. Comparison of degassed (by three freeze–pump–thaw cycles) and nitrogen-purged solutions gave agreement within experimental error.

Gas chromatography was performed on a Hewlett-Packard 5750 dual-flame gas chromatograph. A 6-ft by $^1/_8$-in. column containing 5% SF-96 on chromosorb G was used for most GC analysis. Alternative columns included at 6-ft by $^1/_8$-in. column containing 7% Apiezon L and 2% KOH on chromosorb G, 8% Carbowax 1000/1% KOH on chromosorb G, or 3% OV-101 on Supelcoport.

Preparative Irradiations. All preparative irradiations were performed as follows except where noted. Arene carbonitrile (~70–80 mg) and amine were dissolved to 25 mL in the required solvent. The solution was purged with nitrogen and irradiated using a 450-W Hanovia mercury lamp with a Pyrex filter in a cool water bath. Irradiation was halted at >90% conversion of nitrile, as determined by GC analysis. An aliquot was reserved for GC/MS analysis. The volatile material was removed by rotary evaporation from the remainder of the solution. Thick-layer chromatography of the residual oil (Woelm GF silica, 1000 μm, 5% ethyl acetate in hexane) afforded the products. Deuterium incorporation into reduction and substitution products was determined by comparison of NMR spectra to nondeuterated standards and was confirmed by GC/MS. Deuterium incorporation into recovered starting material was determined by GC/MS.

Solvents. Benzene (Aldrich spectrophotometric grade) was refluxed overnight over P_2O_5 and distilled. The middle 70% was retained and distilled from sodium as required. Acetonitrile (Burdick & Jackson), cyclooctane (Aldrich), and diethyl ether (Malinckrodt, anhydrous grade) were distilled from sodium prior to use. Cyclohexane (Malinckrodt) was distilled from lithium tetrahydroaluminate prior to use. Sulfolane (Aldrich) was distilled from KOH at 1 torr prior to use. Ethyl acetate (Aldrich, spectrophotometric grade), pentane (Aldrich, spectrophoto-

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metric grade), and hexanes (Aldrich, spectrophotometric grade) were used without further purification.

Amines. Diethylamine (Aldrich) was distilled from NaOH prior to use. Diethylamine-*N-d* was prepared by twice exchanging diethylamine with a 5-fold excess of D_2O (Aldrich, 99.8 atom % D), the amine being distilled from the D_2O each time. The product was dried over barium oxide and distilled. This procedure resulted in >97% deuteration (by NMR).

Di(ethyl-*1*-d_2)amine. Lithium tetradeuterioaluminate (Ventron, 1.00 g) was covered with bis(2-ethoxyethyl) ether (freshly distilled from lithium tetrahydroaluminate) under nitrogen. Diacetamide (1.25 g) was dissolved in 40 mL of bis(2-ethoxyethyl) ether and added dropwise to the vigorously stirred tetradeuterioaluminate slurry while cooling in an ice bath. The resulting slurry was heated to 70 °C for 3.5 h and then hydrolyzed by successive addition of 0.4 mL of H_2O, 0.4 mL of 15% NaOH, and 1.2 mL of H_2O followed by stirring overnight. The solution was filtered and distilled from NaOH. The distillate was evaporated under vacuum and the $(CH_3CD_2)_2NH$ was collected in a dry ice/isopropanol trap: 0.481 g; 50.7%; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 6 H), 1.30 (s, 1 H); GC/MS showed one fraction; mass spectrum (EI, 70 eV), *m/e* 77 (34), 62 (100).

Arenecarbonitriles. 9-Phenanthrenecarbonitrile (Aldrich) was recrystallized four times from absolute ethanol. 9-Anthracenecarbonitrile (Aldrich) was recrystallized twice from benzene and sublimed. α-Phenylcinnamonitrile was prepared from benzaldehyde and benzyl cyanide[33] and was recrystallized three times from absolute ethanol prior to use. 3,9- and 3,10-Phenanthrenedicarbonitrile were prepared by the method of Caldwell et al.[18a]

Authentic Samples. *N*-Ethylideneethylamine was synthesized according to the method of Tiollais.[34] It was found that improved yields were obtained when the condensations of amines with the corresponding carbonyl compounds were executed in the freezer (<0 °C). Tetraethylhydrazine was prepared by the method of Nelsen, Peacock, and Weisman.[35] 9,10-Dihydrophenanthrene-9-carbonitrile (I) and 9,10-dihydroanthracene-9-carbonitrile (IV) were prepared by the method of Harvey, Fu, and Rabideau.[36] *N,N*-Diethyl-9-phenanthrenamine (III) was prepared by the method of Kauffmann et al.[37]

Irradiation of 9-PCN with diethylamine in benzene solution was performed by the standard procedure. The resulting light yellow solution was reduced under a stream of nitrogen, placed under vacuum (0.6 torr) for 1 h, and dissolved in $CDCl_3$. The formation of 9-(diethylamino)-9,10-dihydrophenanthrene-9-carbonitrile (II) was confirmed by ^{1}H NMR: δ 7.14–7.81 (m, 8 H), δ_1 3.46, δ_2 3.22 (AB quartet J = 15.8 Hz, 2 H), 2.56 (q, J = 7.1 Hz, 4 H), 0.70 (t, J = 7.1 Hz, 6 H). The formation of *N*-ethylideneethylamine was also indicated by NMR analysis. The solution was chromatographed to afford 9,10-dihydro-9-phenanthrenecarbonitrile (I) [^{1}H NMR ($CDCl_3$) δ 7.14–7.81 (m, 8 H), 4.03 (t, J = 7.7 Hz, 1 H), 3.17 (q, J = 7.7 Hz, 2 H); mass spectrum (EI, 70 eV), *m/e* 205 (100), 178 (29.4)] and *N,N*-diethyl-9-phenanthrenamine (III) [^{1}H NMR ($CDCl_3$) δ 7.29–8.63 (m, 9 H), 3.23 (q, J = 7.1 Hz, 4 H), 1.08 (t, J = 7.1 Hz, 6 H); mass spectrum (EI, 70 eV), *m/e* 249 (41), 234 (100), 204 (60), 178 (39)]. The NMR and mass spectra of I and III were identical with those of independently synthesized materials.

Irradiation of 9-PCN with diethylamine-*N-d* in benzene solution was performed as for diethylamine. NMR analysis in $CDCl_3$ revealed products similar to those obtained with diethylamine except that the AB quartet of the adduct (II) is reduced in intensity by 50%, indicating stereorandom incorporation of 1 equiv of deuterium at the C-10 position. The solution was chromatographed to afford III (with the C-10 resonance decreased in intensity by 50%) and I (with the triplet at δ 4.03 decreased in intensity by 42% and the quartet at δ 3.17 reduced in intensity by 54%).

Irradiation of 9-PCN with Di(ethyl-*1*-d_2)amine in benzene solution by the standard procedure affords III (with α deuterated ethyl groups) and I (with the triplet at δ 4.03 reduced in intensity by 10% and the quartet at δ 3.17 reduced by 22.5%).

Irradiation of 9-ACN with diethylamine in benzene solution was performed by the standard procedure except that the solution was reduced under a stream of nitrogen, dried under vacuum (0.6 torr), and dissolved in $CDCl_3$. NMR analysis demonstrated the formation of 9-(diethylamino)-9,10-dihydroanthracene-9-carbonitrile (V) [δ 6.97–7.88 (m, 8 H), δ_1 4.43, δ_2 3.71 (AB quartet, J = 16.4 Hz, 2 H), 2.50 (q, J = 7.2 Hz, 4 H), 0.64 (t, J = 7.2 Hz, 6 H)]. Chromatography yielded 9,10-dihydro-9-anthracenecarbonitrile (IV) [^{1}H NMR ($CDCl_3$) δ 7.34 (br s, 8 H), 5.01 (s, 1 H), 3.94–4.01 (m, 2 H)] and *N,N*-diethyl-9-anthracenamine (VI) [^{1}H NMR ($CDCl_3$) δ 6.86–8.38 (m, 9 H), 3.55 (q, J = 7.2 Hz, 4 H), 1.06 (t, J = 7.2 Hz, 6 H); mass spectrum (EI, 70 eV), *m/e* 249 (68), 234 (100), 204 (51), 179 (29)].

Irradiation of 9-ACN with diethylamine-*N-d* in benzene solution was performed as with diethylamine. ^{1}H NMR analysis of V gave a similar spectrum except for changes in the AB quartet. The resonance at δ 4.43 was reduced in intensity by 33% and the resonance at δ 3.81 was reduced in intensity by 67%. Assignment of the δ 3.81 resonance to the proton syn to the diethylamino group was made by analogy to the results of Marshal et al.[38] *N,N*-Diethyl-9-anthracenamine (VI) (with the resonances around δ 7.6 diminished 80%) and 9,10-dihydro-9-anthracenecarbonitrile (IV) (with the δ 5.01 resonance decreased in intensity by 5.5% and the multiplet at δ 3.94–4.01 reduced in intensity by 51%) were isolated upon chromatography.

Irradiation of α-CCN with diethylamine in pentane solution by the standard procedure affords *N,N*-diethyl-1,2-diphenylethanamine (VIII) [^{1}H NMR ($CDCl_3$) δ 7.27–8.68 (m, 11 H), 3.25 (q, J = 7.0 Hz, 4 H), 1.10 (t, J = 7.0 Hz, 6 H)] and 2,3-diphenylpropionitrile (VII) [^{1}H NMR ($CDCl_3$) δ 7.12–7.82 (m, 10 H), 4.03 (t, J = 7.6 Hz, 1 H), 3.16 (d, J = 7.6 Hz, 2 H); mass spectrum (EI, 70 eV), *m/e* 207 (25), 206 (80), 205 (100)].

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Registry No. I, 56666-55-8; II, 87871-24-7; III, 25943-35-5; IV, 32319-26-9; V, 87871-25-8; VI, 87871-26-9; VII, 3333-14-0; VIII, 87871-27-0; 9-PCN, 2510-55-6; 9-ACN, 1210-12-4; α-CCN, 2510-95-4; diethylamine, 109-89-7.

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