less acidic -OH group the five-membered ring becomes more unstable which is even more so in the case of the basic amino group. The very interesting finding that molecular hydrogen is formed under anaerobic conditions will be quantitatively investigated in further studies.

Experimental Section

Spectra. The flash apparatus used has been described elsewhere.[11] Uv absorption spectra were measured at room temperature with a Zeiss RPQ 20 spectrophotometer, at low temperatures a Cary 14 spectrophotometer with a thermostated cell holder essentially as described by Fischer,[12,13] *et al.*, was employed.

Compounds. The solvents used were uv grade (Uvasol Merck). All compounds were synthesized using methods described in the literature. Benzylidene-*o*-hydroxyaniline[14] (mp 92°, lit. mp 95°) was recrystallized from ethanol, benzylidene-*o*-aminoaniline[15] (mp 61°, lit. mp 60–61°) was recrystallized from ligroin, and 2-phenylbenzthiazoline[10] (mp 82°) was recrystallized from an ethanol–water mixture and MCH.

Photoproducts in gram amounts were prepared by the illumination of 1 to 2 g of educt in 250 ml of solvent. A high-pressure 125-W Osram mercury lamp was immersed into the stirred, water cooled solution. The photoproducts were recrystallized and showed no mixture melting point depression with authentic samples.

The qualitative determination of hydrogen was carried out with a Perkin-Elmer F7 gas chromatograph using a 5-Å molecular sieve column. About 100 ml of a 0.05 *M* solution of educt in MCH was bubbled with oxygen-free nitrogen for 1 hr and then irradiated with a mercury resonance lamp for 12 hr. The reaction vessel was connected to the gas chromatograph and the gas phase above the reaction mixture analyzed. In blind experiments with the pure solvent negligible amounts of hydrogen were formed.

Hydrogen peroxide was quantitatively determined with $TiOSO_4$. The illuminated solution of Schiff base in MCH was shaken with the acidic aqueous titanium sulfate solution and after separation of the two solvents into two layers the optical density of the orange TiO_2^{2+} solution was determined. In blind experiments it was shown that the hydrogen peroxide is quantitatively transferred into the aqueous phase.

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Reaction Patterns and Kinetics of the Photoconversion of *N*-Methyldiphenylamine to *N*-Methylcarbazole[1a]

E. W. Förster,[1b] K. H. Grellmann,*[1b] and Henry Linschitz[1c]

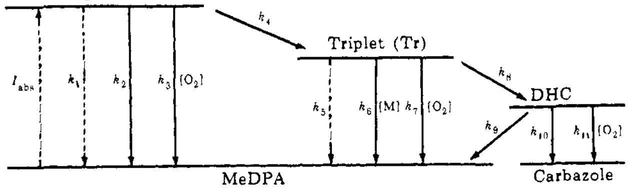
Contribution from the Max-Planck-Institut für Biophysikalische Chemie,
D-3400 Göttingen, Germany, and the Department of Chemistry,
Brandeis University, Waltham, Massachusetts. *Received September 23, 1972*

Abstract: The photoconversion of *N*-methyldiphenylamine (MeDPA) to *N*-methylcarbazole (C) has been studied by steady illumination measurements of carbazole quantum yields and flash photolytic measurements of transient yields and decay kinetics, in degassed and aerobic solution, from room temperature to −140°. The results establish that the reaction proceeds *via* the amine triplet (Tr), which transforms into another intermediate, absorbing at 610 nm, and assigned to *N*-methyl-4a,4b-dihydrocarbazole (DHC). This transient may either revert back to amine or react aerobically or anaerobically to form carbazole. The complex dependence of carbazole and dihydrocarbazole yield on oxygen concentration and temperature is discussed. The processes Tr → DHC and DHC + O_2 → C are demonstrated by flash photolysis, despite unfavorable overlapping absorptions in the latter case. Extinction coefficients of Tr and DHC are obtained, and four rate constants which are involved in the kinetics above −140° are determined directly by flash photolysis. The results are closely consistent with a diffusion-controlled rate for oxygen quenching of the amine triplet. Activation energies are: Tr → DHC, $E_A = 5.5$ kcal mol^{-1}; DHC → MeDPA (ring opening), $E_A = 17.0$ kcal mol^{-1}. The interesting anaerobic reaction DHC → carbazole, with $E_A < 100$ cal mol^{-1}, is discussed.

The oxidative photocyclization of diphenylamines to carbazoles is a complex reaction whose detailed steps exhibit some remarkable kinetic features. However, despite much research, there is still debate and confusion regarding the general reaction scheme. Before any of the interesting mechanistic problems can be treated, it is necessary to resolve these disagreements.

In earlier publications on the photoconversion of *N*-methyldiphenylamine (MeDPA) and triphenylamine to the corresponding carbazoles,[2] the reaction pattern in Scheme I was proposed for the overall process (the broken arrows (k_1 and k_5) indicate unimolecular transi-

Scheme I



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(1) (a) A substantial fraction of this work forms part of a Ph.D. thesis by E. W. F. submitted to Stuttgart University and carried out at the Max-Planck-Institut für Biophysikalische Chemie, Göttingen. Other parts of this work were supported by a grant from the U. S. Atomic Energy Commission to Brandeis University (No. AT (30-1-2003). (b) Max Planck-Gesellschaft Predoctoral Fellow, 1968–1971. (c) Guggenheim Fellow, 1971–1972.

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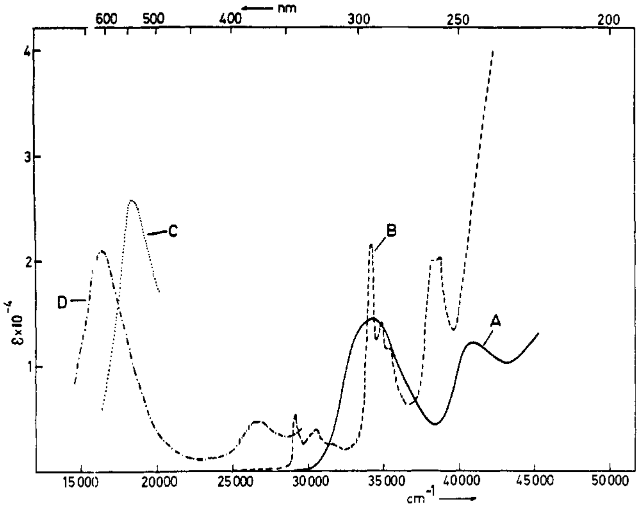
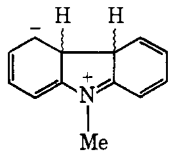


Figure 1. Absorption spectra in methylcyclohexane (A, B, and D) and EPA (C): (A) *N*-methyldiphenylamine at +20°, (B) *N*-methylcarbazole at +20°, (C) triplet absorption spectrum of *N*-methyldiphenylamine at −155°, (D) *N*-methyl-4a,4b-dihydrocarbazole at +20°. The ratio $\epsilon_{DHC}/\epsilon_{Tr}$ has been determined at −155°, ϵ_{DHC}, however, at +20° (see Experimental Section). Curve C was drawn under the assumption that ϵ_{DHC} does not change with temperature.

tions, including fluorescence and phosphorescence emission). This scheme includes two sequential intermediates, the triplet state (Tr) of the amine and another species, seen in flash photolysis and absorbing at 610 nm. For reasons which are further discussed later, this "610" transient was assigned to the *N*-methyl-4a,4b-dihydrocarbazole (DHC). DHC can



DHC

either revert back to parent diphenylamine by the ring opening reaction, k_9, or react to form the carbazole *via* both anaerobic (k_{10}) and aerobic (k_{11}) pathways.

This pattern was proposed to explain the observed dependence of carbazole quantum yield[2b,3] and triplet and DHC lifetimes on oxygen concentration and temperature as well as the sequences of triplet, DHC, and carbazole absorption seen in flash experiments.[2b] Other workers have since repeated and extended some of our measurements and essentially confirmed our observations. However, differences of interpretation have arisen. For example, Shizuka and coworkers have used the above reaction pattern to calculate rate constants and activation energies for the various steps from measurements of carbazole yield as a function of temperature and concentration of oxygen, sensitizers, and quenchers.[4,5] However, on the basis of room temperature flash experiments, they conclude that the "610" transient cannot be identified with the DHC precursor of carbazole. Kemp, *et al.*, have observed the 610 band in pulse radiolysis of triphenylamine solutions but take this species to be the amine triplet.[6] Others[7] have seen both triplet and 610 absorption in flash photolysis of triphenylamine but leave open the possibility that these transients are formed simultaneously rather than sequentially. Sveshnikova and Snegov[8] conclude that the photocyclization of MeDPA proceeds in equal amounts through singlet and triplet intermediates, while Hinohara[9] has proposed that the triplet may not be involved at all.

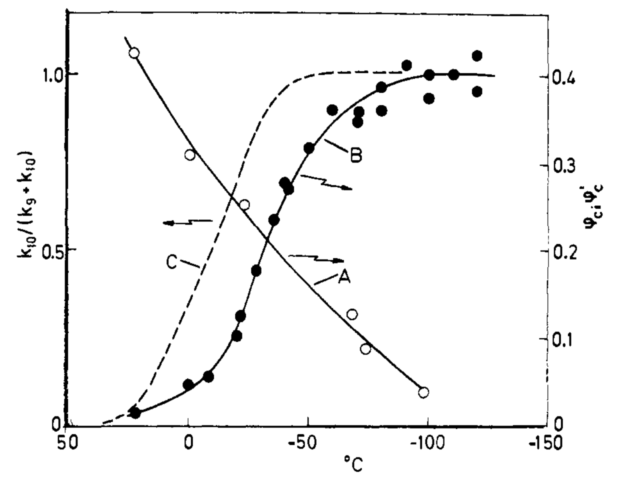


Figure 2. Quantum yields of *N*-methylcarbazole formation as a function of temperature. Solvent, MCH: (A) directly measured in air-saturated solution, (B) directly measured in degassed solution, (C) calculated from the ratio $k_{10}/(k_9 + k_{10})$. The values for k_9 and k_{10} were taken from Figure 4a (*cf.* section 2c).

In order to clarify the situation and to help identify problems which still remain, we present here a more detailed and coherent account of our work than has hitherto been given, together with the results of further studies which appear to us to be definitive in establishing and refining the above reaction scheme. While this paper deals mainly with MeDPA, the general reaction pattern is typical for a wide variety of diphenyl- and dinaphthylamines.[10]

Results and Discussion

1. Carbazole Quantum Yields. Illumination of MeDPA in fluid solvents leads to *N*-methylcarbazole, easily identified by its characteristic absorption spectrum (Figure 1B). The peak at 343 nm (decadic molar extinction coefficient, ϵ = 5800 cm^2 mol^{-1}) does not overlap with reactant absorption (Figure 1A) and is convenient for quantum yield determinations. The cyclization proceeds in a wide variety of solvents (methylcyclohexane (MCH), ethanol, EPA, silicone oil) and in both degassed and aerated media. However, the quantum yields of the aerobic (φ_C') and anaerobic (φ_C) reactions have quite different temperature dependence, as shown in Figure 2. In MCH, air saturated at room temperature, φ_C' decreases steadily from 0.42 at room temperature to 0.04 at −100°. In degassed MCH, φ_C is quite small at room temperature (about 0.01), rises

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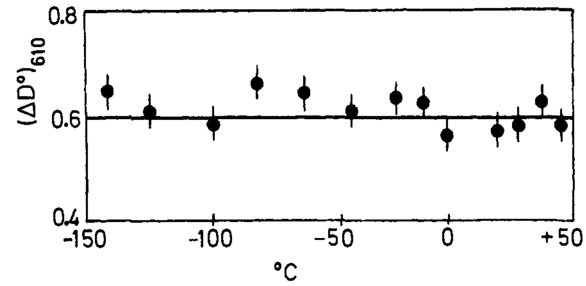

Figure 3. Change of optical density at 610 nm, $(\Delta D^0)_{610}$, after flashing a 2×10^{-4} *M* degassed solution of MeDPA in MCH (+50 to −100°) and 3-methylpentane (−120 and −140°) at different temperatures in a quartz cell of 10-cm optical path length. The values given are extrapolated to zero time (see text).

between 0 and −50° to a very broad maximum ($\varphi_c^{\max} = 0.40$) between −100 and −140° and drops again toward zero below −160°.[2b,3,5] (Our earlier results,[2b] $\varphi_c' = 0.3$ at room temperature and $\varphi_c \sim 0.2$ at −70°, are too low, because of a systematic calibration error.) These measurements are in good qualitative agreement with, but are somewhat lower than, the results of Shizuka, *et al.*[4,5] This seems to be partly, but not entirely, due to the different value (ϵ = 3900 cm² mol⁻¹) taken by Shizuka for the *N*-methylcarbazole 343-nm extinction coefficient. (The lower ϵ appears to correspond to the value in ethanol rather than MCH.)

2. **610-nm Flash Transient. Spectrum, Anaerobic Yield, and Decay Kinetics. A. Spectrum.** Flash illumination of MeDPA in aerated or degassed solvents and at temperatures down to −140° produces the transient species whose spectrum is shown in Figure 1D. In addition to the main band at 610 nm, a broad low maximum occurs around 370 nm, overlapping the long-wave carbazole absorption peak.

B. Anaerobic DHC Yield. Under constant conditions of amine concentration and flash intensity and at temperatures such that the transient is formed rapidly compared to the flash duration ($T > -100°$, see below), the relative yield of DHC is measured by the initial change in absorbance $(\Delta D^0)_{610}$ immediately following the excitation flash. Since the transient lifetime ($\tau >$ 40 msec) is much longer than the flash duration (7 μsec) good values of ΔD^0 are obtained. It is found that the anaerobic DHC yield is essentially constant from 20 to −140° (Figure 3). Below this temperature the yield falls off and at −180° no DHC is seen. This behavior may be understood in terms of the relative temperature dependence of the various pathways by which the amine triplet decays.[2b] As shown below, k_8 is much faster than k_5 or $k_6[\mathrm{M}]$ down to −140°, so that above this temperature all triplet (with temperature independent yield) leads to DHC.

C. Anaerobic DHC Decay Kinetics and Formation of Carbazole. Determination of k_9 and k_{10}. The constancy of DHC yield between 20 and −140° (Figure 3) must be reconciled with the strong variation in anaerobic carbazole yield over this same temperature range (Figure 2B). This may be done on the basis of the temperature dependence of 610 transient decay.

In the absence of oxygen, DHC disappearance is accurately first order, with lifetimes of about 40 msec at room temperature, increasing to 1 sec at −30°. However, below −30°, the anaerobic decay becomes remarkably independent of temperature.[2b] Figure 4A gives an Arrhenius plot of the first-order DHC transient decay rate in various solvents. It is apparent that two sharply different processes are involved. The first reaction, which controls the anaerobic decay at high temperatures, gives a good Arrhenius line, with activation energy of 17 kcal mol⁻¹. As the temperature is lowered, this decay path gives way to a second, temperature-independent process, which becomes rate controlling below −30°. Comparing the anaerobic decay rate and carbazole quantum yield (Figures 2B, 2C, 4A and 4C), it is evident that the rise in φ_C with decreasing temperature corresponds qualitatively with the transition from the first to the second mode of DHC decay. Accordingly, we identify the temperature-dependent process as the ring-opening back reaction, DHC → MeDPA, for which we find (Figure 4A)

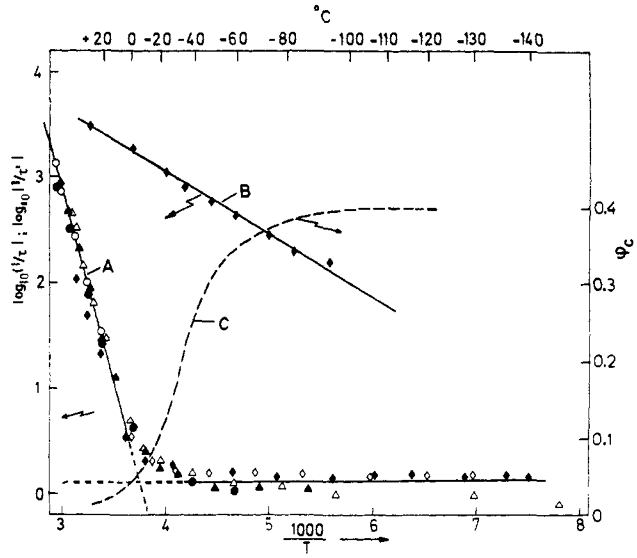

Figure 4. Arrhenius plot of the decay of DHC monitored at 610 nm in different solvents: (A) degassed solution ($1/\tau$), (B) air-saturated solution ($1/\tau'$): (◆) ethanol, (△) 3-methylpentane, (◊) EPA 5:5:2, (▲) MCH, (●) silicone oil, (○) hexadecane. For comparison the anaerobic carbazole quantum yield, φ_C (*cf.* Figure 2), is shown as a function of $1000/T$ (dashed line, curve C).

$$k_9 = 10^{14} \exp(-17{,}000/RT)\ \mathrm{sec}^{-1}$$

The striking temperature-independent anaerobic decay, rate limiting at low temperatures and associated with high carbazole yield, is assigned to a rate-controlling step in the reaction DHC → carbazole. For this process, Figure 4A gives

$$k_{10} = 1.2\ \mathrm{sec}^{-1}\ (E_{10} < 0.10\ \mathrm{kcal\ mol}^{-1})$$

Thus, in degassed solution above −140°, when the DHC yield is constant, φ_C is controlled by competition between k_9 and k_{10}. These results constitute very strong evidence that the 610 transient is a direct intermediate in anaerobic carbazole formation.

3. **Aerobic DHC Decay Kinetics and Yield; Formation of Carbazole and Determination of k_{11}. A. Kinetics.** Oxygen accelerates the disappearance of the 610 transient and in excess leads to accurate pseudo-first-order decay kinetics. Figure 4B gives an Arrhenius plot for the decay in ethanol, air-saturated at room temperature. At this oxygen concentration and from room temperature to −100°, the aerobic decay is very much faster than the anaerobic rate, and essentially all

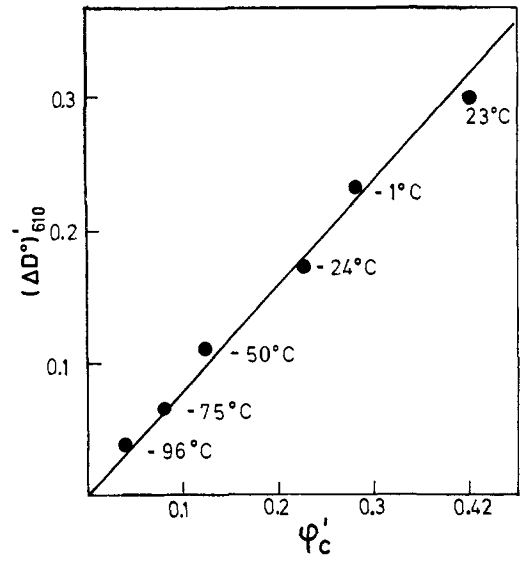

Figure 5. Change of optical density at 610 nm, $(\Delta D^0)'_{610}$, after flashing a 2×10^{-4} *M* solution of MeDPA in a quartz cell of 10-cm optical pathlength *vs.* carbazole quantum yield φ', both in air-saturated MCH at corresponding temperatures.

DHC is trapped by the oxygen reaction. The line of Figure 4B thus represents the temperature variation of k_{11}. Taking $[O_2] = 2.3 \times 10^{-3}$ *M*,[5,11] we obtain

$$k_{11} = 1.2 \times 10^8 \exp(-2800/RT)\ M^{-1}\ \text{sec}^{-1}$$

B. Aerobic Yields of DHC and Carbazole. The relative yield of DHC in the presence of oxygen was again measured by the initial transient absorbance as found by extrapolation of the decay curve back to zero time after the flash. In sharp contrast to the anaerobic situation, it is found that the aerobic DHC yield, proportional to $(\Delta D^0)'_{610}$, falls steadily as the temperature is lowered. This effect may be understood (see below) as the result of increasing, diffusion-controlled oxygen quenching of the amine triplet (k_7) relative to its more strongly temperature-dependent cyclization to DHC, k_8.

The decrease in aerobic DHC yield with temperature closely parallels the fall in aerobic carbazole quantum yield (Figure 2A). This correspondence is shown in Figure 5, in which the initial flash absorption change $(\Delta D^0)'_{610}$ at a given temperature is plotted against the steady illumination value of φ_C' measured at the same temperature. It is seen that the two yields are proportional to each other over the entire temperature range. This is in accord with our reaction scheme, since at high oxygen concentration, where all DHC decays *via* the rapid aerobic pathway, $k_{11}[O_2]$ (Figure 4B), the carbazole yield should be controlled simply by the initial DHC yield. We conclude that the 610 transient is an intermediate leading to carbazole in the aerobic as well as anaerobic reactions.

The "610" species is assigned a dihydrocarbazole structure for three reasons. First, its appearance as intermediate in diphenylamine cyclization resembles other labile species observed in related oxidative cyclization[12,13] and reversible photochromic reactions.[14] Second, the ring-opening back reaction, "610" → MeDPA, has an activation energy close to that of similarly assigned processes in dihydrophenanthrenes.[14] Third, the absorption at 610 nm is reasonable, for a system of five conjugated double bonds, in a charge-resonance zwitterion structure (DHC).

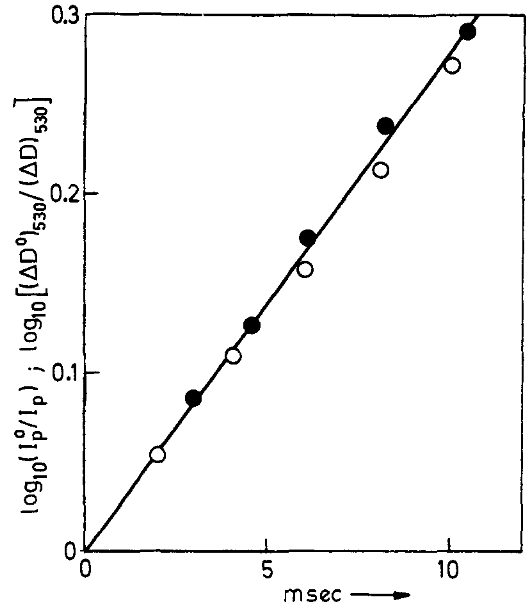

Figure 6. Comparative decay of transient (triplet) absorbance at 530 nm (dark circles), and phosphorescence emission at 430 nm (open circles), following flashing of 1×10^{-4} *M* MeDPA (temperature −155°, solvent ethanol).

4. The Triplet State of MeDPA and Formation of DHC. Determination of k_7 and k_8. In rigid media at liquid nitrogen temperatures, MeDPA phosphoresces strongly at 430 nm[5] and neither DHC nor carbazole is formed.[2b,5] As the temperature is raised above −150° both 610 transient absorption and (anaerobic) carbazole formation develop, and the phosphorescence intensity diminishes. However, at these low temperatures, the 610 absorption is not the first flash transient to be seen. Instead, below −100° a new initial transient appears absorbing at 540 nm (Figure 1C) whose first-order decay rate (measured at −155°) closely matches both the decay of 430 nm phosphorescence emitted from the fluid solution (Figure 6) and the growing-in of the 610-nm band[15] (Figure 6 and Figure 7c). We conclude that the 540-nm intermediate is the MeDPA triplet, and that this gives rise to DHC at temperatures above −150°. Similar results have been obtained in low-temperature flash experiments on triphenylamine.[2,7,10]

The triplet lifetime decreases strongly with increasing temperature. Above −100°, the 540 transient is too short-lived to be detected by standard flash photolytic means, and 610 is the only intermediate seen, but laser techniques permit the triplet decay to DHC to be followed up to room temperature.[15] In degassed solution, the rise in DHC yield with increasing temperature and particularly the constant yield above −150° (Figure 3) indicates that this shortening of triplet lifetime is

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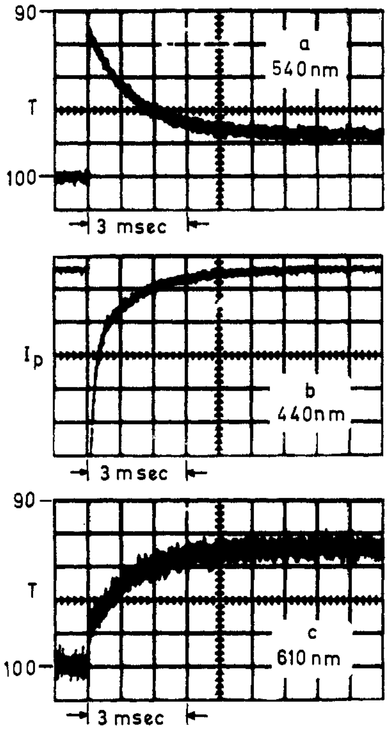

Figure 7. Oscilloscope traces after flashing a 2 × 10^{-4} *M*, degassed solution of MeDPA in ethanol at −155°. Vertical scale, per cent transmission (*T*) or phosphorescence intensity (I_p) in arbitrary units; time scale, 1 msec/div: (a) decay of the amine triplet at 540 nm, overlapped by the slow decay of DHC (horizontal part of the curve); (b) decay of the amine phosphorescence at 440 nm (the steep part at the very beginning of the curve is due to flash stray light); (c) growing-in of DHC at 610 nm overlapped by the amine triplet absorption (fast rise of the curve at the very beginning).

caused essentially by the increase in rate of DHC formation, k_8. Figure 3 shows that already at −140° k_8 must be fast enough to dominate the two competing triplet decay processes, first-order radiative and radiationless transition to the ground state (k_5), and pseudo-first-order triplet quenching by adventitious quenchers (k_6[M]). In agreement with this, an activation energy of 5.5 kcal mol^{-1} is obtained from an Arrhenius plot of the first-order rate constant for triplet (540 nm transient) decay, over the temperature range (−140 to −100°) in which the lifetime is accessible to direct flash photolytic measurement (Figure 8, open circles). This value is considerably higher than that expected for k_5 and k_6 but is in accord with the cyclization of amine triplet to DHC. From Figure 8, we obtain

$$k_8 = 8 \times 10^{11} \exp(-5500/RT) \text{ sec}^{-1}$$

The high frequency factor of k_8 implies that DHC is first formed in its *triplet* state, and direct evidence for this has already been given by means of laser photolysis.[16]

Terry, *et al.*, have particularly remarked on the anomalously large temperature sensitivity of the triphenylamine triplet lifetime.[7] This phenomenon arises, as is now apparent, from the existence of the temperature-dependent decay pathway, k_8, leading to DHC. Other substituted diphenylamines, which are highly photostable, form neither carbazoles nor DHC and show "normal" lifetime–temperature behavior.[15,17]

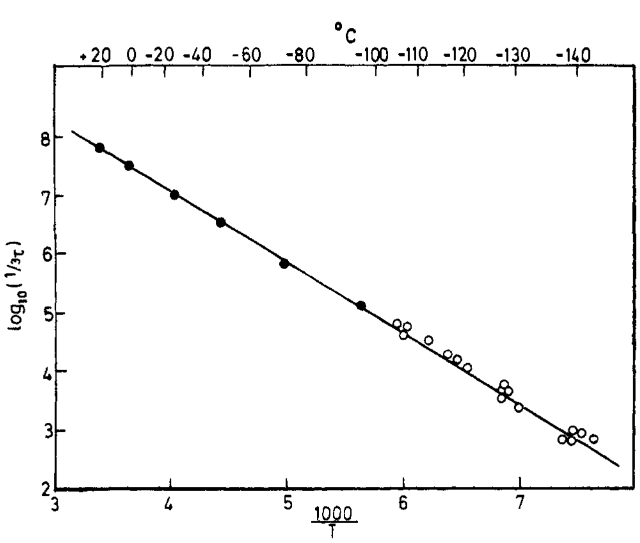

Figure 8. Arrhenius plot of MeDPA triplet decay ($1/{}^3\tau$): dark circles—values calculated from eq 3, solvent MCH; open circles—directly measured by flash photolysis, solvent ethanol.

Further information regarding k_7 and k_8 is given by the effect of aerobic *vs.* anaerobic conditions on the yield of DHC at various temperatures (Figures 3 and 5). Oxygen will influence φ_{DHC} by competitive quenching of both the singlet and triplet states of the amine. Also, at constant flash intensities and amine concentrations, φ_{DHC} is proportional to $(\Delta D^0)_{610}$. Therefore, using primes to denote solutions containing oxygen

$$\left(\frac{\varphi'}{\varphi}\right)_{\mathrm{DHC}} = \frac{(\Delta D^0)'_{610}}{(\Delta D^0)_{610}} = \frac{k_4{}^1\tau'}{k_4{}^1\tau}\,\frac{k_8{}^3\tau'}{k_8{}^3\tau} \qquad (1)$$

whence

$$\frac{{}^3\tau'}{{}^3\tau} = \frac{(\Delta D^0)'_{610}}{(\Delta D^0)_{610}}\,\frac{\varphi_{\mathrm{F}}}{\varphi_{\mathrm{F}}'} \qquad (2)$$

The ratio $\varphi_{\mathrm{F}}/\varphi_{\mathrm{F}}'$ is about 1.10 for air-saturated MCH at room temperature[4] and rapidly becomes even closer to unity as the temperature is lowered. We therefore take this factor to be unity over the entire range. Hence

$$\frac{(\Delta D^0)'_{610}}{(\Delta D^0)_{610}} = \frac{k_5 + k_6[\mathrm{M}] + k_8}{k_5 + k_6[\mathrm{M}] + k_7[\mathrm{O_2}] + k_8} \qquad (3)$$

Above −140° k_5 and k_6[M] are much smaller than k_8 and may be neglected. Thus, using the measured DHC yield ratio, we may determine $k_7[\mathrm{O_2}]$ from k_8 at low temperatures, where k_8 is directly measurable. At higher temperatures, where k_8 is too fast to be measured, we may assume k_7 to be diffusion controlled and evaluate k_8 thereby.

We first consider the high temperature case, −100 to +20°. The diffusion-controlled rate constant was taken to be[18] $k_7(T) = 3 \times 10^{10}\ (\eta_{20}/\eta_T)\ M^{-1}\ \mathrm{sec}^{-1}$, where η_{20} and η_T are the solvent viscosities at 20 and *T*°, respectively.[19] In air-saturated MCH, $[\mathrm{O_2}] = 2.3 \times 10^{-3}\ M$,[5,11] and Figure 3 gives $(\Delta D^0)_{610} = 0.60$ at all temperatures above −140°. The observed variation of $(\Delta D^0)'_{610}$ with temperature is given in Figure 5 and extends over about a tenfold range.[20]

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[20] At −100° in air-saturated MCH $(\Delta D^0)'_{610}/(\Delta D^0)_{610}$ is 0.05, from which we conclude that at least 95% of the DHC molecules are generated from the triplet state.

The triplet lifetimes $^3\tau$ thus obtained in the temperature range -100 to $+20°$ and in MCH solvent are shown in the Arrhenius plot of Figure 8 (dark circles). These values agree very well with those extrapolated from direct flash photolysis measurements of k_8 in ethanol, in the lower temperature range (Figure 8, open circles). This agreement, corresponding to the use of eq 3 at lower temperatures to obtain k_7 from directly measured triplet lifetimes, confirms the overall consistency of our assumptions, as well as the value given by Ware for the oxygen quenching rate constant at room temperature.[18] Indeed, the excellent Arrhenius line (Figure 8), covering a variation in the rate constant of five orders of magnitude, is perhaps the best evidence that in degassed solution the triplet decays by only one pathway, k_8, throughout the range considered, in accord with our interpretation of the results of Figure 3.

Further evidence that carbazole is formed *via* the triplet is, of course, the sensitization of the reaction by triplet donors[4,21] and its inhibition by triplet quenchers.[4,10] It is noteworthy that the sensitized reaction also involves DHC formation. Flashing a solution of 10^{-2} *M* propiophenone and 10^{-3} *M* MeDPA using filtered excitation (Schott WG 360, 2 mm) absorbed only by the ketone gave DHC transients in expected amounts. No DHC was formed in similar blank experiments, omitting the sensitizer.

5. Rate of Formation of Carbazole by Flash Photolysis. The most direct evidence that DHC is the carbazole precursor would be the flash-photolytic observation of growing-in of carbazole absorption at a rate equal to the disappearance of the 610 transient. However, at room temperature and in air-saturated MCH solution, the absorbance at 341 nm shows simply a sharp rise, coincident with the flash, and no further growth corresponding to 610 decay (Figures 9a and 9b). On this basis, doing flash experiments only at room temperature and apparently assuming that all 341-nm absorption must be assigned to carbazole, Shizuka, *et al.*, have concluded that the 610 transient cannot be identified with the dihydrocarbazole intermediate in the reaction.[5] This argument neglects the possibility of overlapping absorption between decaying precursor and growing-in product. In fact, above 300 nm, DHC absorption is within experimental error everywhere greater than carbazole (as shown by decreasing rather than increasing transient absorption) except at 341 nm, where an isosbestic region exists (see below). The difficulty of resolving the 343-nm carbazole peak is increased by the rather wide monochromator slits needed in flash work. (The bandwidth in this wavelength region is about 5 nm.) Thus, in the presence of oxygen, the absorption at 341 nm remains stationary after the flash as 610 decays and carbazole grows in (Figures 9a and 9b). However, reliable correction may be made for the overlapping absorption by first establishing the complete DHC spectrum under conditions where very little carbazole is formed, *i.e.*, in degassed solution at room temperature where k_9 is rate controlling. In this case, the transient decay at 610 nm is identical with that at 341 nm (Figures 9e and 9f). Since only one species appears, we may determine the relative extinction coefficients at these wavelengths. The DHC initial absorption and its decay at

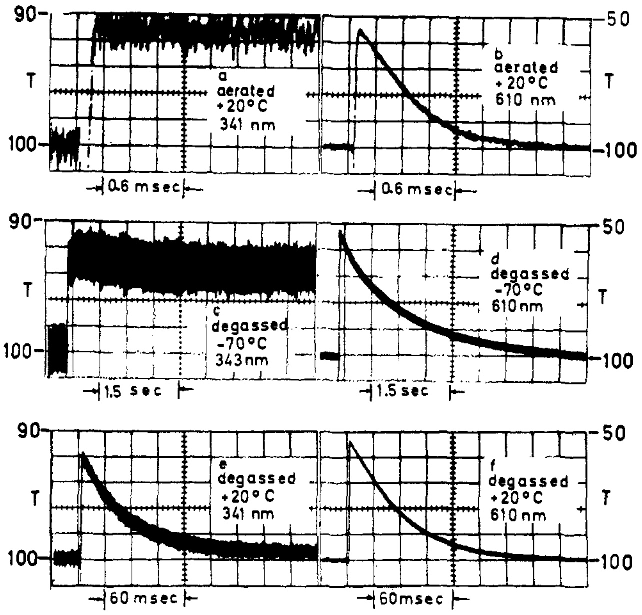

Figure 9. Oscilloscope traces after flashing a 2×10^{-4} *M* solution of MeDPA in MCH. Vertical scale, per cent transmission (*T*). The flash intensity in the aerated samples (a and b) was twice as high as in the degassed samples (c, d, e, and f) to make the traces directly comparable.

341 nm can thus be obtained even in aerobic solution from the measured absorption changes at 610 nm, where there is no overlap. Deducting this 341-nm absorption from the flash profile of Figure 9a, we find that for *aerobic* solutions the initial ΔD^0_{341} corresponds *solely* to DHC formation, and that "product" absorption grows-in exponentially at a rate equal to DHC disappearance. Moreover, the irreversible increase in absorption (Figure 9a) corresponds to the amount of carbazole formed as determined spectrophotometrically after a number of flashes. A direct *sequential* relationship is thus established between the two species, DHC and carbazole. From the above results, we also determine the absolute extinction coefficients of DHC (Figure 1). This was done by comparing $(\Delta D^0)'_{610}$ per flash with the total carbazole production in aerobic solution at room temperature. Since the triplet decays quantitatively to DHC in degassed MCH, we may then estimate the triplet extinction (Figure 1) from low-temperature oscilloscope traces by comparing the initial (triplet) ΔD^0 with the residual absorption of the relatively long-lived DHC (Figures 7a and 7c). (For details see the Experimental Section.)

6. DHC and Triplet Quantum Yields. Thus far, we have discussed the yields of DHC and triplet only in relative terms, based on relative intensities of the flash transients. In view of the results given here, we may now safely exclude the formal possibility that these species are produced in side reactions parallel to carbazole formation[5,8] and proceed to determine their absolute yields.

In air-saturated MCH, above $-100°$, we have seen that all DHC disappears *via* the oxygen reaction, $k_{10}[O_2]$, leading to carbazole (Figures 4B and 5). Since at room temperature $\varphi'_C = 0.42$, it follows that $\varphi'_{DHC} \geqslant 0.42$. Under steady illumination, the aerobic room temperature reaction leads to excellent isosbestic points.[1] The spectra are composed only of the amine and carbazole, and hydrogen peroxide is formed in

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[21] E. Tauer, Masters Thesis, Erlangen, 1966.

stoichiometric amounts.[21] Thus, the aerobic conversion of DHC to carbazole involves little or no side reaction and we take $\varphi'_{DHC} = \varphi'_C = 0.42$ at 20°.

Comparing the amount of DHC formed by equal flash intensities in degassed and aerated solutions at room temperature, we find $(\Delta D^0)_{610}/(\Delta D^0)'_{610} = 2.0$, so that in degassed solution, where triplet quenching by oxygen does not compete, $\varphi_{DHC} \sim 0.84$. As shown by Figure 3, this yield remains constant down to $-140°$. We have established that in this temperature range, all triplet decays to DHC. Hence, above $-140°$, $\varphi_{DHC} = \varphi_{T_T} = 0.84$. The quite high triplet yield in MeDPA, determined in this way, is close to that measured for triphenylamine by the stilbene isomerization technique[22] and corresponds to the value given by Shizuka, *et al.*[4] However, this latter agreement is fortuitious, arising from the combined effects of a carbazole quantum yield different from ours and a different choice of rate constant for diffusion-controlled oxygen quenching.[4] The sum (0.88) of triplet and fluorescence yields ($\varphi_F = 0.04$)[3,4] seems to differ significantly from unity and it appears that a small amount of radiationless transition from the excited singlet also occurs ($\varphi_{S_1 \rightarrow S_0} \sim 0.12$).

7. **Nature of the Anaerobic Reaction.** Making the steady-state assumption our reaction scheme leads to eq 4 for the carbazole quantum yield in the an-

$$\varphi_C = \frac{k_4}{k_1 + k_2 + k_4} \frac{k_8}{k_5 + k_6[M] + k_8} \frac{k_1}{k_9 + k_{10}} \quad (4)$$

aerobic case. At all temperatures above $-140°$ the first factor of eq 4 is the constant triplet yield, $\varphi_T = 0.84$, the second factor is essentially unity in this temperature range (Figure 3; $\varphi_{DHC} = 0.84$), and so φ_C should vary as the third factor, $k_{10}/(k_9 + k_{10})$. Figure 2 compares the temperature dependence of the function $k_{10}/(k_9 + k_{10})$ with that of the experimental φ_C. It is seen that the rise in carbazole yield with decreasing temperature occurs at a somewhat lower temperature than corresponds simply to the suppression of k_9. This focuses attention on the details of the very interesting anaerobic DHC → carbazole reaction.

The rate constant, k_{10}, is characterized by an extraordinarily low-frequency factor and essentially zero energy of activation. We have proposed earlier[2b] that this process might be a tunnelling reaction, eliminating molecular hydrogen. However, contrary to reports on the situation in diphenylamine,[3] no H_2 formation is observed in MeDPA photolysis (amounts less than 1% of theoretical should have been detected in experiments using a McLeod gauge).[23] Also, the values of k_9 and k_{10} are identical for both ordinary and perdeuterio-MeDPA.[23] Thus, elimination of H_2 cannot account for k_{10}, and, in the absence of explicitly added oxidants, it is clearly necessary to identify the hydrogen acceptor in the reaction.

The limiting low-temperature value of φ_C shows that despite the strictly first-order character of k_{10} about half of the DHC, in the most favorable case, must be transformed into a product other than carbazole. These kinetic and yield results suggest therefore that k_{10}, with its remarkable kinetic parameters, corresponds to a rate-limiting unimolecular transformation of DHC. This process is then followed, at low temperatures, by a more rapid dismutation reaction resulting in a carbazole yield of about 0.5. At somewhat higher temperatures, we believe other competing processes may occur after the k_{10} transformation, which decrease the carbazole yield still further. The difference between the empirical φ_C and $k_{10}/(k_9 + k_{10})$ curves (Figure 5) thus measures the effect of these side reactions. Further, more definite conclusions require full chemical identification of all the products of the low-temperature anaerobic reaction. This work is well under way.[24]

Experimental Section

Materials. *N*-Methyldiphenylamine (MeDPA) (Eastman Kodak Analytical Grade) was used without further purification. The solvents used were uv grade (Merck Uvasol).

Quantum Yields. The light source was a current-stabilized medium pressure mercury lamp (Osram Hg-3) from which the 313.5-nm line was isolated by means of a high intensity (Bausch & Lomb) monochromator. The absolute quantum yield of *N*-methylcarbazole formation was determined in aerated methylcyclohexane solution at 23°, by ferrioxalate actinometry according to Hatchard and Parker.[25] Carbazole concentrations were calculated from absorption spectra, using a molar decadic extinction coefficient $\epsilon = 5800$ cm^2 mol^{-1} for the *N*-methylcarbazole peak at 343 nm. Quantum yields under other reaction conditions were measured relative to the room temperature aerobic value. For measurements at different temperatures (Figures 2A and B) the photolysis cell (quartz, 1 cm) was thermostated in a copper block, through which was passed a controlled stream of cold nitrogen gas. Temperatures remained constant to within one degree over the whole range studied. The block, containing openings for the passage of light, was supported in a quartz dewar with plane windows. The entire assembly was mounted in the cell compartment of a Cary 14 spectrophotometer and could be rotated 90° to permit either photolysis (through an aperture in the sidewall of the cell compartment) or measurement of the absorption spectrum of the solution. The reference cell was kept at room temperature. In blank experiments the baseline was found to be constant at all temperatures over the entire spectral region. Spectra were recorded at each temperature before illumination and after about 2, 4, 6, 8, and 10% conversion. Within experimental error the quantum yields were independent of exposure time which varied between 2 min and 2 hr, depending on temperature and quantum yield. The relative amounts of carbazole formed were calculated from the recorded spectra by comparing the change in absorbance at 260 and (in aerated solution) 343 nm. The absorbance of the solutions varied between 0.3–0.45 at 313 nm due to solvent contractions and to the fact that the solutions were not made up to exactly the same concentrations. Appropriate corrections were made for the amount of light absorbed.

The carbazole quantum yields in air-saturated solution (Figure 2A) are estimated to be accurate to ±10%. However, because of side reactions which occur in degassed solutions (see section 7) and which are more serious at higher temperatures (-40 to $+20°$), quantum yields in anaerobic solution are less reliable, We assume that the change in absorbance at 260 nm represents only the conversion of *N*-methyldiphenylamine to *N*-methylcarbazole, and that the absorption of side products may be neglected. Thus, the quantum yield values given in Figure 2B are upper limits, which may be 10 to 20% too high between -120 and $-60°$ (section 7) and much too high above $-40°$.

Extinction Coefficients. a. *N*-Methylcarbazole. The extinction coefficient of *N*-methylcarbazole was determined using a carefully purified sample which was photochemically synthesized. MeDPA (3 g in 2 l. of methanol) was illuminated for 8 hr at 23° with an Osram HQA-250 lamp. The solution was aerated every 2 hr. The light-brown product (2.5 g) obtained upon evaporation was vacuum sublimed, recrystalized from methanol three times (white needles, mp 93°, lit.[26] mp 91°), and again vacuum sublimed to avoid inclusions of solvent. At 343 nm $\epsilon = 5800 \pm 50$ cm^2 mol^{-1} in MCH and 4000 ± 100 cm^2 mol^{-1} in ethanol. The low

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[22] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

[23] V. Kasche and H. Linschitz, unpublished observations.

[24] K. H. Grellmann, W. Kühnle, and Th. Wolf, to be published.

[25] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 235, 518 (1956).

[26] R. Storrie and S. H. Tucker, *J. Chem. Soc.*, 2262 (1931).

value in ethanol is accompanied by broadening of the absorption bands.

b. *N*-Methyl-4a,4b-dihydrocarbazole (DHC). A solution of 1.1×10^{-4} *M* MeDPA in air-saturated MCH was flashed 14 times and the change of optical density recorded at 610 nm with the flash apparatus. The oscilloscope traces were extrapolated to zero time $(\Delta D^0)'_{610}$, and the sum compared with the amount of carbazole produced. The latter was calculated from the final absorption spectrum of the flashed solution. The optical density at 343 nm was 0.056 ± 0.001 (1-cm path length) and $\Sigma(\Delta D^0)'_{610}$ was 2.0 ± 0.1 (10-cm path length). In order to avoid a concentration gradient of the transient DHC due to inhomogeneous excitation of the solute, a narrow flash cell 1 × 15 × 100 mm, which has been described elsewhere,[27] was used. The extinction coefficient at 610 nm is $\epsilon_{\mathrm{DHC}} = 21000 \pm 2000$ cm^2 mol^{-1}.

c. MeDPA Triplet State. As shown in section 5, the amine triplet in degassed solution above −140° decays quantitatively to DHC. Therefore the ratio

$$R(\lambda) = \epsilon_{\mathrm{Tr}}(540)/\epsilon_{\mathrm{DHC}}(\lambda) = \Delta D^0{}_{\mathrm{Tr}}(540)/\Delta D^{\infty}{}_{\mathrm{DHC}}(\lambda)$$

where $\Delta D^0{}_{\mathrm{Tr}}$ is the change in optical density at 540 nm of a low temperature amine solution immediately after flashing, corresponding to the triplet, and $\Delta D^{\infty}{}_{\mathrm{DHC}}(\lambda)$ is the residual optical density at wavelength λ, corresponding to the long-lived DHC. If λ is taken to be 540 nm, then both $\Delta D^0{}_{\mathrm{Tr}}$ and $\Delta D^{\infty}{}_{\mathrm{DHC}}$ can be measured on a single oscilloscope trace (Figure 7A). However, $\Delta D^{\infty}{}_{\mathrm{DHC}}(540)$ is rather small and lies on a steep slope of the DHC spectrum. If λ is taken at the DHC maximum, 610 nm, then determination of $R(610)$ requires two flashes and sweeps (Figure 7C) with possible errors arising from variation in flash intensity. The change in amine concentration between successive flashes is negligible at the concentrations used. The average of several measurements at −155° gives $R(540) = 3.0 \pm 0.3$ and $R(610) = 1.25 \pm 0.03$. Using the extinction coefficient ϵ_{DHC} of DHC determined at room temperature we obtain $\epsilon_{\mathrm{Tr}}(540) = 26{,}000 \pm 3000$ cm^2 mol^{-1}. This value is a lower limit because ϵ_{DHC} may be higher at lower temperatures. The experimentally determined isosbestic point at 574 nm and −155° agrees very well with the isosbestic point in Figure 1, where a low temperature spectrum (C) is combined with one measured at room temperature (D), using the ratios $R(\lambda)$ given above. This indicates that the DHC spectrum does not change drastically with temperature.

Preparation of Solutions. For the anaerobic experiments the solutions were thoroughly degassed on a high-vacuum line by standard freeze–pump–thaw technique until stick vacuum on a McLeod gauge was reached. When the effect of oxygen on the reaction was investigated, the solutions were air saturated at room temperature and then cooled down to the desired temperature. In the flash and absorption cells the liquid had only a few square millimeters contact to air and the flash cell was separated from the gas–liquid interface by a long (~100 mm) capillary, filled with solution. We therefore assumed that the oxygen concentration did not change significantly on cooling.

Flash Apparatus. The capacitor energy dissipated through a spark gap and two air-filled (~20 Torr) flash capillary tubes in series was 150 J (0.75 μF, 20 kV). The lifetime, $\tau_{1/2}$, of the flash was 7 μsec with a nonexponential tail of about 20-μsec duration. The detection system consisted of a parallel light beam from a 100-W iodine–quartz lamp which passed through the cylindrical quartz cell of 12-mm i.d. and 100-mm optical path length and which was focussed onto the entrance slit of a 500-mm Bausch & Lomb grating monochromator. Close to the exit slit a 1P28 photomultiplier with cathode follower was mounted. The electrical signal was recorded with a 549 Tektronix storage oscilloscope. The reproducibility of the flash output was better than 5% within a series of measurements.

For the low-temperature experiments the flash cells were mounted horizontally in a quartz dewar with plane end windows. The temperature was regulated by a stream of cold nitrogen[28] and kept constant within ±1°. After the desired temperature was reached in the dewar, the solution was allowed to equilibrate for at least 20 min. When quantum yields obtained from flash experiments are compared (Figures 3 and 5; $(\Delta D^0)_{610}/(\Delta D^0)'_{610}$) the average of at least five independent experiments is given. In cases where the carbazole quantum yield was high (degassed solution at low temperature, aerated solution at room temperature), care was taken to keep the concentration of the reactant always in large excess to avoid appreciable light absorption by the photoproduct.

All absorption spectra were measured on a Cary 14 spectrophotometer.

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