A(4a) = 46.8 G, A(4b) = 45.8, given the assumptions in section V. Although this difference is small (2%), we believe it to be real. Analyses of NADH spectra obtained with other dyes give similar results.[29] A slightly nonplanar geometry of the nicotinamide ring in NADH$^{+\cdot}$ brought about by a stacking interaction with the adenine ring could be responsible.

Acknowledgment. This work was performed at the national NMR facility at the University of Groningen, supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.). P.J.H. is grateful to the Royal Society, London, for the award of a research fellowship.

Registry No. NADH, 58-68-4; 7,8,10-trimethyl-3-carboxymethylisoalloxazine, 20227-26-3.

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(29) Hore, P. J.; Kaptein, R., unpublished results.

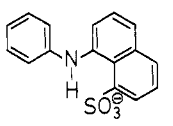
Reactivity and Decay Pathways of Photoexcited Anilinonaphthalenes

K. H. Grellmann* and U. Schmitt

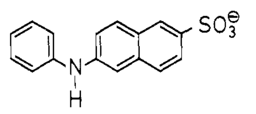
Contribution from the Max-Planck-Institut für biophysikalische Chemie, Abteilung Spektroskopie, D 3400 Göttingen, West Germany. Received March 1, 1982

Abstract: N-Methyl-2-anilinonaphthalene (**2**-MAN) is converted by light into 7-methyl-7H-benzo[c]carbazole (**7**-MBC) and 5-methyl-6,7-dihydro-5H-benzo[c]carbazole (**9**). The reaction takes place only in the absence of oxygen and is regioselective; i.e., the isomeric 5-methyl-5H-benzo[b]carbazole (**5**-MBC) is not formed. Ring closure takes place from the excited triplet state of **2**-MAN and a zwitterionic intermediate was found in flash experiments. N-Methyl-2-anilino-6-naphthalenesulfonate (**2**-MANS) behaves similarly. Caution should therefore be exercised if such compounds are used as fluorescence probes. N-Methyl-1-anilinonaphthalene (**1**-MAN) is photochemically more stable than **2**-MAN.

Anilinonaphthalenes, e.g., **1** and **2**, have been widely used as fluorescence probes for structure studies in biochemistry[1] because the quantum yield and the spectral distribution of the fluorescence of such compounds depend strongly on solvent polarity.

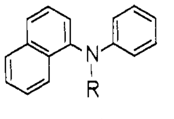


1

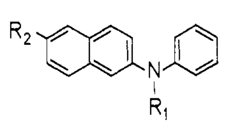


2

Since diphenylamines are by light effectively converted into carbazoles,[2] it is to be expected that anilinonaphthalenes undergo similar photoinduced ring-closure reactions forming benzocarbazoles. Such photoproducts which strongly fluoresce could cause artifacts if the parent compounds are used as fluorescence labels. We therefore investigated the photochemical properties of N-methyl-1-anilinonaphthalene (**1**-MAN) and N-methyl-2-anilinonaphthalene (**2**-MAN) in some detail by means of steady-state and flash experiments. Similar to **1** and **2** the fluorescence spectra and the fluorescence quantum yields of **1**-MAN and **2**-MAN depend strongly on solvent polarity.

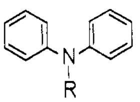


1-MAN (R = CH$_3$)
1-AN (R = H)

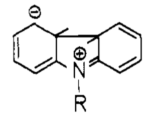


2-MAN (R$_1$ = CH$_3$; R$_2$ = H)
2-AN (R$_1$ = R$_2$ = H)
2-MANS (R$_1$ = CH$_3$; R$_2$ = SO$_3^-$)

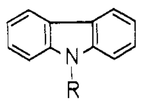
We began our studies with the N-methyl compounds in order to avoid complications due to side reactions which were observed in the case of diphenylamines. For instance, in the presence of oxygen N-methyldiphenylamine (**3**) is converted by light[3] into N-methylcarbazole (**7**) via the zwitterionic dihydrocarbazole intermediate[4] **5**. In the case of **4** side reactions occur[5] due to hydrogen abstraction from the N-H group of the corresponding zwitterion **6**, which reduce the quantum yield of the formation of **8**.



3 (R = CH$_3$)
4 (R = H)



5 (R = CH$_3$)
6 (R = H)



7 (R = CH$_3$)
8 (R = H)

Results

***N*-Methyl-2-anilinonaphthalene (2-MAN). Steady-State Photochemistry and Product Analysis.** Illumination of *degassed* solutions of **2**-MAN in acetonitrile, ethanol, or methylcyclohexane (MCH) results in the formation of 7-methyl-7H-benzo[c]carbazole (**7**-MBC) and 5-methyl-6,7-dihydro-5H-benzo[c]carbazole (**9**) with a total quantum yield of 5-10%. The concentration ratio **7**-MBC:**9** is about 2:1. Both compounds were identified by comparison with authentic samples (mp, UV and NMR spectra). The UV spectra of **2**-MAN before and after illumination together with the spectrum of **7**-MBC, all in acetonitrile, are given in Figure 1. In MCH the absorption spectrum of **7**-MBC is similar to that in acetonitrile but the absorption peaks between 350 and 370 nm

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(1) (a) Radda, G. K. *Curr. Top. Bioenerg.* **1971**, *4*, 81-126. (b) Brand, L.; Gohlke, J. R. *Annu. Rev. Biochem.* **1972**, *41*, 843-68. (c) Radda, G. K.; Vanderkooi, J. *Biochim. Biophys. Acta* **1972**, *265*, 509-49. (d) Träuble, H. *Biomembranes* **1972**, *3*, 197-227. (e) Azzi, A. *Q. Rev. Biophys.* **1975**, *8*, 237-316.

(2) (a) Parker, C. A.; Barnes, W. J. *Analyst (London)* **1957**, *82*, 606-18. (b) Bowen, E. J. Eland, J. H. D. *Proc. Chem. Soc., London* **1963**, 202. (c) Grellmann, K. H.; Sherman, G. M.; Linschitz, H. *J. Am. Chem. Soc.* **1963**, *85*, 1881-2.

(3) Fischer, G.; Fischer, E.; Grellmann, K. H.; Linschitz, H.; Temizer, A. *J. Am. Chem. Soc.* **1974**, *96*, 6267-9.

(4) (a) Förster, E. W.; Grellmann, K. H. *J. Am. Chem. Soc.* **1972**, *94*, 634-5. (b) Förster, E. W.; Grellmann, K. H. *Chem. Phys. Lett.* **1972**, *14*, 536-8. (c) Förster, E. W.; Grellmann, K. H.; Linschitz, H. *J. Am. Chem. Soc.* **1973**, *95*, 3108-15.

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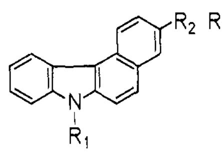
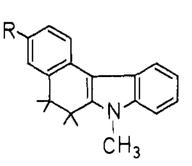
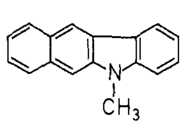


7-MBC ($R_1 = CH_3$; $R_2 = H$)
7-BC ($R_1 = R_2 = H$)
7-MBCS ($R_1 = CH_3$; $R_2 = SO_3^-$)



9 (R = H)
10 ($R = SO_3^-$)

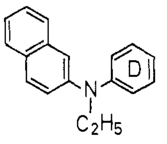


5 - MBC

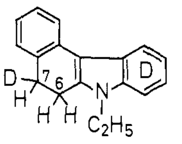
are sharper in MCH (cf. Figure 3).

In air-saturated solution **2**-MAN is much more stable. The quantum yield of **2**-MAN disappearance is 10–20 times smaller than in degassed solutions. Only small amounts of **7**-MBC are formed. The main part of the reaction mixture consists of other photoproducts which were not identified.

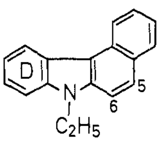
The ring-closure reaction of **2**-MAN is remarkably regioselective. The isomer 5-methyl-5*H*-benzo[*b*]carbazole (**5**-MBC) could not be detected in the reaction mixture. We estimate that the NMR detection limit is 0.5% of **5**-MBC contained in **7**-MBC (cf. Figure 2). Some static illumination experiments were carried out with the partially deuterated amine *N*-ethyl-2-(pentadeuterioanilino)naphthalene (**2**-EAND). (The *N*-ethylamine was



2 - EAND



11



7 - EBCD

used because it is easier to synthesize than the *N*-methyl derivative.) The NMR spectra of the photoproducts **11** and **7**-EBCD show that the dihydrocarbazole **11** contains three protons at C-6 and C-7 and one deuteron either at C-6 or at C-7. We were not able to deduce from the NMR spectra whether the D atom is located at C-7 (as shown in the formula) or at C-6.

The carbazole **7**-EBCD contains only hydrogen atoms in the naphtho group and only deuterium atoms in the benzo group. It does, therefore, not arise from **11** (via dehydrogenation) because in this case part of the **7**-EBCD molecules should contain deuterium at C-5. More than 5–10% of such a compound (or of any other isomer) would have been detected in the NMR spectra.

The dihydrocarbazole **9** is in degassed as well as air-saturated solutions converted by light into **7**-MBC without side reactions (Figure 3). In air-saturated solution the quantum yield of this reaction is 5–7 times higher than in the absence of oxygen.

Flash Photolysis. Two transient absorptions ($\lambda_{max} = 500$ nm and $\lambda_{max} = 620$ nm) were observed after flash excitation of **2**-MAN dissolved in degassed MCH. In Figure 4 the absorption spectra of the two transients are shown. The decay of the transient with $\lambda_{max} = 500$ nm is first order and at 294 K its lifetime $\tau_t = 120$ μs. An Arrhenius plot of $1/\tau_t$ between 344 and 153 K shows (cf. Figure 5) that two processes with rate constants $k_2 = (2.3 \times 10^5\ s^{-1}) \exp(-8.4\ kJ\ mol^{-1}/RT)$ and $k_3 = (6.1 \times 10^{11}\ s^{-1}) \exp(-49.2\ kJ\ mol^{-1}/RT)$ are responsible for the decay of the transient. At low temperatures solutions of **2**-MAN in MCH–isopentane strongly phosphoresce (λ_{max} = 494, 505, 532, 548 (shoulder), 577, 625 (weak shoulder) nm). At 81 K the phosphorescence lifetime $\tau_p = 1.4$ s. At higher temperatures (100–160 K) τ_p was determined in flash experiments and found to be in excellent agreement with τ_t. We therefore assign the transient with $\lambda_{max} = 500$ nm to the triplet state of **2**-MAN. The low-frequency factor ($T_1 \rightarrow S_0$ transition) and the low activation energy (adventitious quenching) of k_2 corroborate this assignment. (The decay process with rate constant k_3 will be discussed below.) The yield of triplet formation ($\phi_t(T)$) was found to be constant between 150 and 300 K (cf. Figure 6). The yield of the second transient ($\lambda_{max} = 620$ nm) decreases strongly at lower temperatures (cf. Figure 6). Its decay could therefore only be analyzed above 280 K. It is of mixed first and second order. Only the rate constant of the first-order process, $k_5 = [(4 \pm 2) \times 10^9\ s^{-1}] \exp(-60 \pm 3\ kJ\ mol^{-1}/RT)$, could be determined fairly accurately from an Arrhenius plot because the accurate determination of the second-order rate constant required a better signal-to-noise ratio[6] than we were able to obtain in our flash experiments. In air-equilibrated MCH solutions ($[O_2] = 2.3 \times 10^{-3}$ M) the triplet state is quenched by oxygen with a quenching constant $k_q = 8 \times 10^9\ M^{-1}\ s^{-1}$ (295 K); the second transient is not at all observed in air-equlibrated solutions.

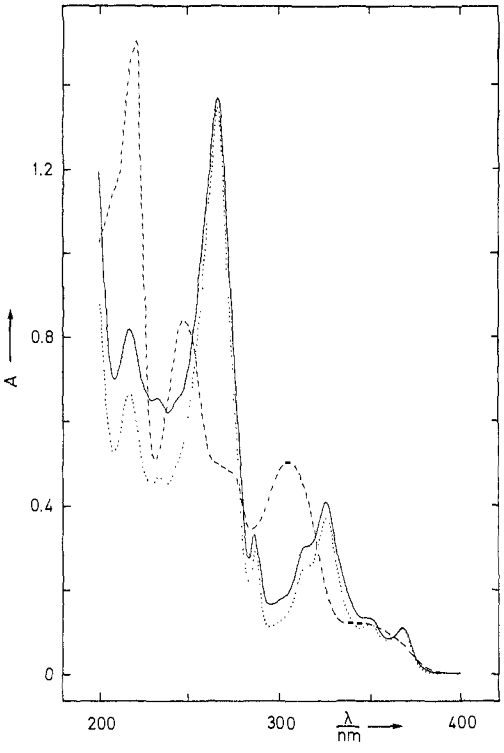


Figure 1. Absorption spectrum of 3×10^{-5} M **2**-MAN in degassed MCH before (dashed line) and after (solid line) illumination with a medium-pressure Hg lamp through a 345-nm cutoff filter. For comparison the spectrum of an authentic sample of **7**-MBC (dotted line) is also shown.

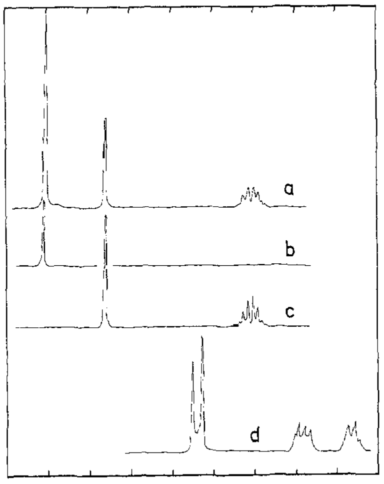


Figure 2. NMR (270 MHz) spectra. Solvents: CD_3CN (a–c), D_2O (d). Standards: Me_4Si (a–c), TSP-d_4 (d). a: Spectrum fraction of the reaction mixture obtained after illumination of **2**-MAN in degassed MCH. (Before the spectrum was taken, unreacted **2**-MAN was removed from the photoproducts by column chromatography.) b: Spectrum fraction of an authentic sample of **7**-MBC. c: Spectrum fraction of an authentic sample of the dihydrocarbazole **9**. d: Spectrum fraction of the reaction mixture obtained after illumination of **2**-MANS in degassed ethanol.

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(6) Grellmann, K. H.; Scholz, H. G. *Chem. Phys. Lett.* **1979**, *62*, 64–71.

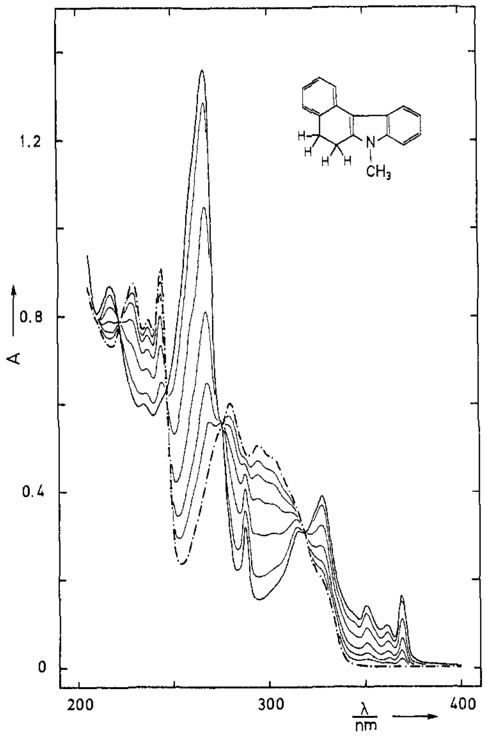


Figure 3. Absorption spectrum of 3.5×10^{-5} M **9** in air-equilibrated MCH before (dashed-dotted line) and after (solid lines) a number of consecutive illumination periods (medium-pressure Hg lamp through a 280-nm cutoff filter).

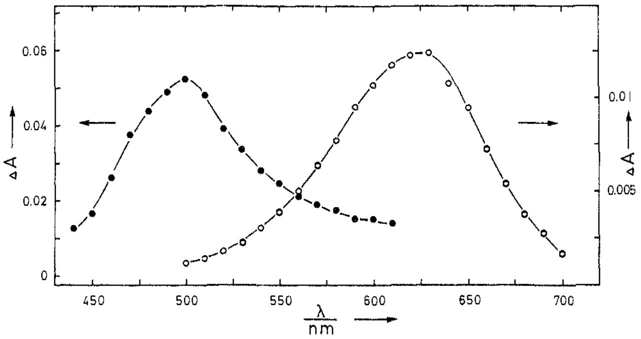


Figure 4. Transient absorption spectra observed after excitation of a solution of 3×10^{-5} M **2**-MAN in degassed MCH with a microsecond flash (half-width of the flash ~ 3 μs); optical path length, 10 cm. Full circles: Triplet-triplet absorption of **2**-MAN at 153 K. The change in absorbance, ΔA (left-hand scale), was determined from first-order decay curves extrapolated to time zero. Open circles: Spectrum of transient Z at 293 K. ΔA (right-hand scale) was determined from decay curves 80 ms after flash excitation.

***N*-Methyl-1-anilinonaphthalene (1-MAN).** **1**-MAN is photochemically much more stable than **2**-MAN in both degassed and air-saturated solutions. The quantum yield of decomposition is 1×10^{-3}–2×10^{-3}. Traces of the corresponding benzocarbazole are formed but the main fraction of the photoproducts consists of unidentified compounds with unstructured UV spectra.

In flash experiments carried out in degassed MCH as solvent we observed only one transient which decays in a first-order reaction (k_t) and which we assign to the triplet state of **1**-MAN. Its lifetime is $\tau_t = 2$ ms in degassed MCH and $\tau_t' = 120$ ns in air-equilibrated MCH at 296 K; i.e., the oxygen quenching constant is $k_q = 4 \times 10^9$ M^{-1} s^{-1}. From an Arrhenius plot of k_t we obtained $k_t = (2 \times 10^4\ \text{s}^{-1}) \exp(-9.1\ \text{kJ mol}^{-1}/RT)$. The absorption spectrum of the transient is shown in Figure 7. At 81 K solutions of 1-MAN in isopentane–MCH (5:1) phosphoresce (λ_{max} = 535, 568, 610 (weak shoulder) nm). The phosphorescence lifetime at this temperature is $\tau_p = 560$ ms. In acetonitrile no phosphorescence is observed.

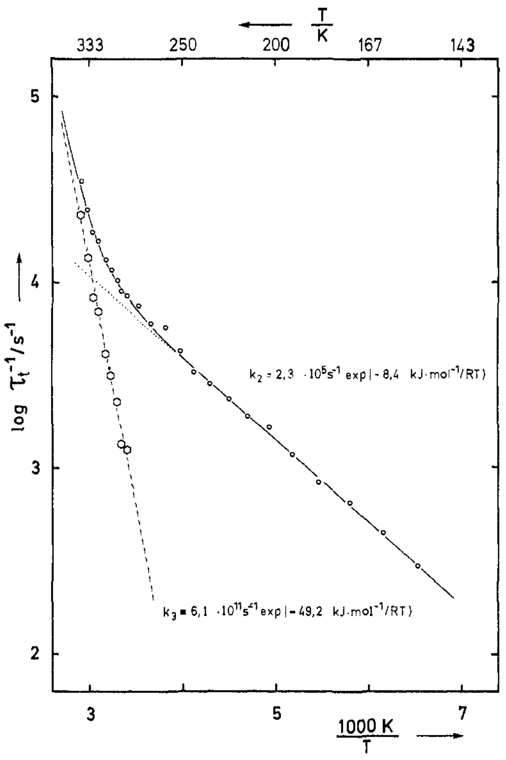


Figure 5. Arrhenius plot of the decay of the **2**-MAN triplet state in degassed MCH, monitored at 490 nm. The rate constant $k_3(T)$ was calculated from the difference $k_3(T) = 1/\tau_t/(T) - k_2(T)$.

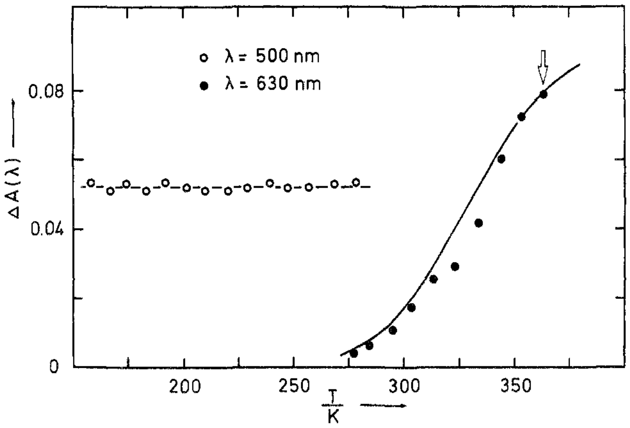


Figure 6. **2**-MAN (1.3×10^{-4} M) in degassed MCH. Absorbance change, $\Delta A(\lambda)$, at different temperatures after flash excitation, caused by the formation of the triplet state of **2**-MAN (open circles, monitoring wavelength λ = 500 nm) and of Z (full circles, λ = 630 nm). The solid line (right-hand curve) was calculated from rate constants (see text) and normalized at 363 K (arrow in Figure 6).

Other Anilinonaphthalenes. 2-Anilinonaphthalene (2-AN). **2**-AN is in degassed solution converted by light into 7*H*-benzo[*c*]carbazole (**7-BC**). The quantum yield of this reaction is lower than in the case of **2**-MAN due to side reactions and it is completely suppressed in air-equilibrated solutions. The side reactions are presumably due to hydrogen abstraction from the N–H group of the primary ring-closure product.

***N*-Methyl-2-anilino-6-naphthalenesulfonate (2-MANS).** **2**-MANS is not soluble in MCH. Under illumination in air-equilibrated ethanol it decomposes slowly into unidentified products with unstructured absorption spectra. Illumination in degassed ethanol leads to the formation of two photoproducts which could not be separated by means of TLC or GC. The NMR spectrum of the reaction mixture shows at high field singlets of two different N–CH_3 groups with an intensity ratio of about 2:1 (cf. Figure 2). The absorption spectrum of the reaction mixture (Figure 8) is very similar to the photoproduct spectrum shown

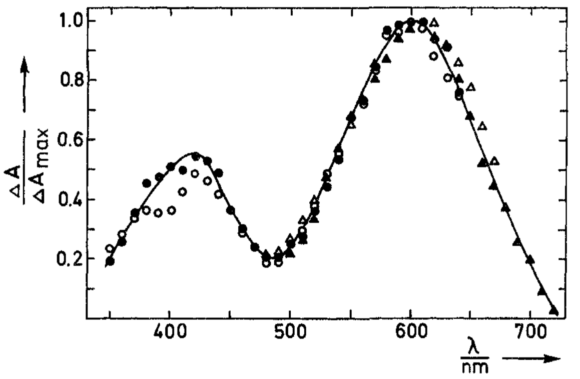


Figure 7. 1-MAN (3×10^{-5} M) in MCH degassed and air equilibrated. Triplet–triplet absorption observed after excitation with a nitrogen laser (flash half-width, 3 ns). Open circles: air-equilibrated solution, 50 ns after excitation. Full circles, open and full triangles: degassed solution 1, 50, and 80 μs after excitation, respectively.

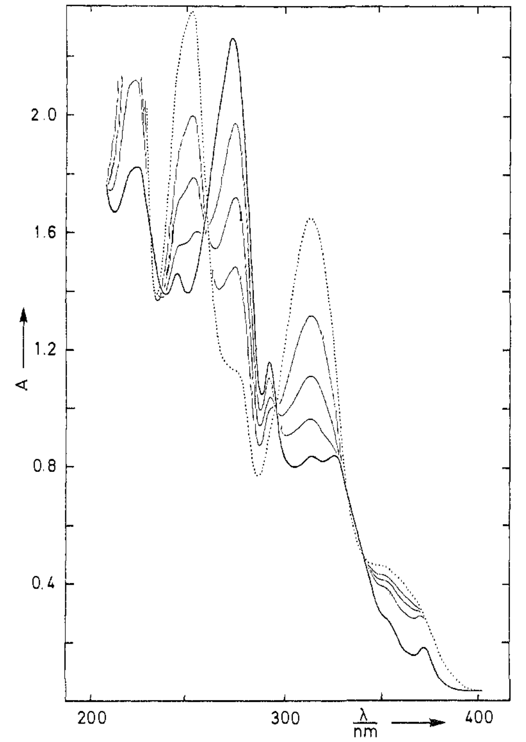


Figure 8. Absorption spectrum of 1×10^{-4} M 2-MANS in degassed ethanol before (dotted line) and after (solid lines) a number of consecutive illumination periods (medium-pressure Hg lamp through a 320-nm cutoff filter).

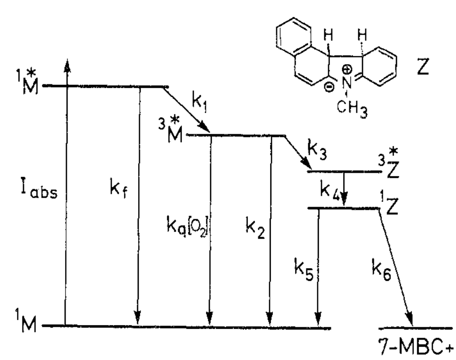
in Figure 1. We therefore conclude that the main photoproduct (~70%) is 7-methyl-7*H*-benzo[*c*]carbazole-3-sulfonate (7-MBCS). The minor product is presumably the corresponding dihydrocarbazole **10**. The total quantum yield is 2–5%.

Flash experiments carried out with 2-MANS in degassed ethanol gave results which are quite similar to those obtained with 2-MAN in degassed MCH. We observed two transient species. One has an absorption maximum at 500 nm and decays in a first-order reaction with a lifetime of 200 μs at 293 K. We assign it to the triplet state of 2-MANS. Yield and lifetime of the second transient (λ_{max} = 630 nm) depend strongly on temperature as in the case of 2-MAN. At 310 K its half-life is about 1 s and its decay is of mixed first and second order. An Arrhenius plot of the first-order process gave the rate constant $k = [(4 \pm 2) \times 10^8\ s^{-1}] \exp(-51 \pm 3\ kJ\ mol^{-1}/RT)$.

Discussion

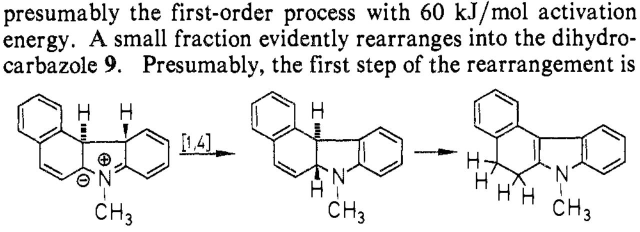
The experimental results presented in this paper indicate that the photochemical conversion of 2-MAN into 7-MBC proceeds in close similarity to the ring-closure reaction of diphenylamines.[4]

Scheme I



We therefore propose the following reaction mechanism (Scheme I). After intersystem crossing from the first excited singlet state $^1M^*$ of 2-MAN (rate constant k_1) into its excited triplet state $^3M^*$ (which competes with the radiative process (k_f)), ring closure occurs to the zwitterionic intermediate, Z, in its singlet ground state, ^1Z (k_3 and k_4), with the quantum yield ϕ_z. One of the resonance structures of Z is inserted in Scheme I. Competing with the ring-closure reaction (k_3) is the "normal" triplet deactivation (k_2) and quenching ($k_q[O_2]$) if oxygen is present. According to Scheme I the temperature dependence of the quantum yield ϕ_z in degassed solution is given by $\phi_z(T) = \phi_t k_3(T)/(k_2(T) + k_3(T))$. Since the quantum yield of 2-MAN triplet formation, ϕ_t, is temperature independent (cf. Figure 6), the relative yields $\phi_z(T)/\phi_z(363\ K)$ can be calculated from the rate constants $k_2(T)$ and $k_3(T)$ (solid line in Figure 6) and compared with the relative yields, $\Delta A_{630}(T/\Delta A_{630}(363\ K)$ determined directly from the change of absorbance at 630 nm (ΔA_{630}) immediately after flash excitation at different temperatures, T (full points in Figure 6). The satisfactory agreement of the data shows that the assignment of the process with low activation energy (cf. Figure 5) to the normal triplet decay (k_2) is correct and that the process with high activation energy (k_3) leads to the formation of Z. The large frequency factor of k_3 indicates that the ring-closure reaction takes place adiabatically in the triplet manifold. In contrast to *N*-methyldiphenylamine where the formation and the decay of the zwitterionic intermediate in its excited triplet state, $^3Z^*$, could be seen in nanosecond flash experiments[4b] (in this case $k_3 = 2 \times 10^7\ s^{-1}$ at 293 K), we did not find such an intermediate in the case of 2-MAN. This is presumably due to the relatively small rate constant k_3 (for instance, $k_3 = 1 \times 10^3\ s^{-1}$ at 293 K) which might be the rate-determining step of the $^3Z^*$ decay. If $k_3 < k_4$, no measurable concentration of $^3Z^*$ can accumulate and the transient Z can only be observed in its singlet ground state ^1Z. Since below 300 K ^1Z is formed only with low yield (cf. Figure 6), the growing-in of the Z spectrum can only be observed at higher temperatures where $k_3 > k_2$. At 340 K and above the buildup of the ^1Z absorption (monitored at 620 nm) was observed. It matches exactly the decay of the amine triplet absorption (monitored at 480 nm).

The decay of ^1Z is a rather complicated process. Part of ^1Z reverts by ring opening (k_5) to the starting material. This is presumably the first-order process with 60 kJ/mol activation energy. A small fraction evidently rearranges into the dihydrocarbazole **9**. Presumably, the first step of the rearrangement is



^1Z 12 9

a sigmatropic 1,4 hydrogen shift, in analogy to the rearrangement reactions of enamines.[7] The resulting dihydrocarbazole **12** is

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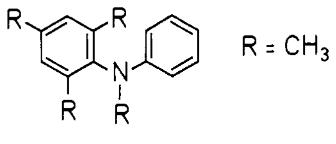
[7] (a) Chapman, O. L.; Eian, G. L.; Bloom, A.; Clardy, J. *J. Am. Chem. Soc.* **1971**, *93*, 2918–28. (b) Grellmann, K. H.; Kühnle, W.; Wolff, Th. *Z. Phys. Chem. (Frankfurt am Main)* **1976**, *101*, 295–306.

apparently not stable and rearranges further to yield **9**.

The mechanism of the dehydrogenation reaction $^1Z \rightarrow$ **7-MBC** is not known. We have no experimental evidence that the second-order part of the ^1Z decay is a disproportionation reaction as it was observed with *N*-methyldiphenylamine[8] because in the mass spectra of the reaction mixture we could not find a tetrahydrocarbazole, i.e., a mass two units higher than that of **2-MAN**. Since tetrahydrocarbazoles are quite often very labile compounds and since low-temperture experiments cannot be carried out with **2-MAN** because of the decreasing yield ϕ_z (cf. Figure 6), it will be very difficult to investigate this part of the reaction in more detail.

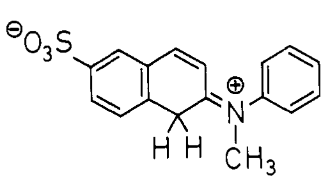
The relatively long lifetime of the amine triplet state is the reason that **7-MBC** formation is not observed in air-equilibrated solutions because $k_q[O_2] \gg k_3$. For instance, at 293 K the ring-closure rate constant $k_3 = 1 \times 10^3$ s^{-1}, but $k_q[O_2] = 1.6 \times 10^7$ s^{-1}. Recently, it has been suggested[9] that the angle of twist between the naphthyl and phenyl rings of **2-MAN** is responsible for the nonreactivity of this compound and the triplet quenching by oxygen was considered to be unimportant, which is not correct. One could, perhaps, argue that a large angle of twist is the reason for the low value of k_3. However, with the trimethyl derivative **13** of *N*-methyldiphenylamine in which the two phenyl rings are certainly twisted the ring closure to the corresponding zwitterionic transient proceeds even faster[8] (about 10 times) than with the parent amine.



13

We feel that the electron density distribution in the excited triplet state governs this reaction and causes also its regioselectivity. This interesting aspect of the reaction mechanism will be discussed in more detail elsewhere together with the photoreactions of other relevant diphenylamine derivatives.

The results obtained with the sulfonated compound **2-MANS** are very similar to those reported for **2-MAN**. Therefore, the reaction mechanism outlined above for **2-MAN** can also be applied to **2-MANS**. In particular, the great similarity of the absorption spectra of the photoproducts (cf. Figures 1 and 8) leaves little doubt that the main photoproduct of **2-MANS** irradiation is the benzocarbazole **7-MBCS**. Dodiuk and Kosower published a photoproduct spectrum[10] obtained from irradiation of **2-MANS** in ethanediol which is practically identical with the absorption spectrum in Figure 8. Relying on NMR data these authors proposed for the photoproduct the imine structure **14**. In our experiments carried out in degassed ethanol two products were formed which could not be separated on chromatographic columns, presumably due to the highly polar sulfogroup. Therefore, the NMR spectrum of the reaction mixture is rather complicated. It can, however, be compared with the spectra of the authentic samples of **7-MBC** and **9** a small part of which is shown in Figure 2. We see no reason to assume that in ethanol compound **14** is formed and we are convinced that **7-MBCS** is the main photoproduct. Since the absorption spectra of the photoproducts in ethanol and in ethanediol are identical, there remains little doubt that the assignment of Dodiuk and Kosower is not correct. We also suspect that in a kinetic study[11] the properties of **7-MBCS** rather than of **14** were investigated.



14

1-MAN does not form **5-MBC** upon illumination. Consequently, one observes in flash experiments only the triplet state of **1-MAN** but no zwitterionic intermediate. Only one position in the naphthalene moiety of this molecule is available for a ring-closure reaction. Its nonreactivity is presumably due to an unfavorable electron density distribution in the excited state.

Kinetic studies in the nanosecond[12a] and, especially, in the picosecond[12b] time range clearly demonstrated that **1-AN** and its derivatives can be used as fluorescence probes only with caution. Obviously, **2-AN** derivatives are even worse candidates for such studies because additional problems may arise due to their facile conversion into benzocarbazoles under anaerobic conditions.

Experimental Section

Materials. *N*-Methyl-1-anilinonaphthalene (1-MAN). 1-Anilinonaphthalene (6.67 g, 0.03 mol) and 5.7 mL (0.06 mol) of dimethylsulfate were kept for 1 h at 100 °C. Then 7.6 g (0.135 mol) of KOH in 40 mL of H_2O was added and refluxed for 2 h. The reaction mixture was extracted with 2 × 50 mL of diethyl ether, and the extract dried with Na_2SO_4 and evaporated. The residue was chromatographed on Al_2O_3 with cyclohexane–CCl_4 1:1: yield 0.68 g (0.003 mol); mp 43 °C (lit.[13] 52–53 °C); correct elemental analysis; UV$_{max}$ (log ϵ) in methylcyclohexane (MCH) 337 (3.46), 288 (3.81), 250 (4.23) nm. The lit.[13] mp for **1-MAN** and **2-MAN** (see below) seem doubltful because the elemental analyses reported in ref 13 deviate strongly from the calculated values.

***N*-Methyl-2-anilinonaphthalene (2-MAN).** 2-MAN was prepared from 2-anilinonaphthalene like 1-MAN: mp 53 °C (lit.[13] 88–90 °C); correct elemental analysis; UV$_{max}$ (log ϵ) in MCH 347 (3.61), 306 (4.20), 277 (4.15), 248 (4.41) nm; NMR (Me_2SO-d_6) δ 7.78 (d), 7.75 (d), 7.75 (d), 7.42 (t), 7.38 (s), 7.33 (t), 7.33 (t), 7.31 (t), 7.17 (d), 7.11 (d), 7.11 (d), 7.02 (t), 3.38 (s, 3 H).

3,4-Dihydro-1*H*-naphthalen-2-one Phenylhydrazone (15). **15** was prepared from phenylhydrazine and 3,4-dihydro-1*H*-naphthalen-2-one (β-tetralone) in 50% acetic acid, mp 109–110 °C (lit.[14] 109 °C).

6,7-Dihydro-5*H*-benzo[*c*]carbazole (16). **15** (5 g, 0.021 mol) was dissolved in 75 mL of ethanol and under stirring 2.5 mL of concentrated H_2SO_4 in 25 mL of ethanol was slowly added. To the red solution 400 mL of H_2O was added and the solution was neutralized with 30% NaOH. A dark resin precipitated. Recrystallization from petrol ether (bp 60–80 °C) afforded 1.7 g (0.0078 mol) of colorless crystals, mp 100.5–101 °C (lit.[15] 100 °C).

5-Methyl-6,7-dihydro-5*H*-benzo[*c*]carbazole (9). **16** (0.5 g, 0.0023 mol) was dissolved in 10 mL of acetone and 0.5 g (0.0089 mol) of ground KOH added. After 10 min 0.5 g (0.0035 mol) of CH_3I and after 15 min 20 mL of H_2O were added. The reaction mixture was extracted with diethyl ether, and the extract dried with Na_2SO_4 and evaporated. Recrystallization from petrol ether (bp 40–60 °C) afforded 0.27 g (0.0016 mol) of colorless crystals: mp 133.5 °C; NMR (CD_3CN) δ 8.00 (d), 7.82 (d), 7.43 (d), 7.27 (t), 7.26 (d), 7.20 (m, 2 H), 7.06 (t), 3.72 (s, 3 H), 3.02 (m, 4 H).

***N*-Ethyl-2-(pentadeuterioanilino)naphthalene (2-EAND).** *N*-Acetyl-2-naphthylamine (3 g, 0.016 mol), 10 g (0.06 mol) of bromobenzene-d_5, 1.5 g (0.01 mol) of K_2CO_3, a trace of Cu powder, and KI were heated to 210 °C for 1 h. Water and unreacted bromobenzene were evaporated under vacuum, and the residue was dissolved in 150 mL of ethyl ether, filtered, dried with Na_2SO_4, and reduced with $LiAlH_4$. The product was purified on a Al_2O_3 column with cyclohexane–diethyl ether 1:1: yield 0.5 g (0.002 mol); UV$_{max}$ in MCH 350, 310, 278 nm; NMR (CD_3CN) δ 7.75 (d), 7.69 (d), 7.69 (d), 7.4 (t), 7.36 (s), 7.3 (t), 7.14 (d), 3.88 (q, 2 H), 1.23 (t, 3 H).

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7-Methyl-7*H*-benzo[*c*]carbazole (7-MBC). 2-MAN (0.233 g, 0.001 mol) was dissolved in 1 L of UV-grade cyclohexane. The solution was illuminated in a Rayonet RPR-100 reactor for 15 h with "350-nm" lamps. Thirty minutes before and during illumination purified N_2 was bubbled through the solution. After evaporation of the solvent the residue was chromatographed on a SiO_2 column with cyclohexane-toluene 1:1. Two fractions (starting material and photoproduct) were collected. The photoproduct (7-MBC) was recrystallized twice from methanol and afforded 17 mg (7.4×10^{-5} mol) pale yellow crystals: mp 118 °C (lit.[17] 118-119 °C); UV_{max} (log ϵ) in MCH 369 (3.90), 362 (3.58), 350 (3.77), 327 (4.21), 315 (4.06), 288 (4.09), 267 (4.77) nm; NMR (Me_2SO-d_6) δ 8.80 (d), 8.62 (d), 8.09 (d), 8.01 (d), 7.93 (d), 7.77 (d), 7.72 (t), 7.52 (t), 7.48 (t), 7.36 (t), 4.02 (s, 3 H).

Irradiation. Spectroscopic irradiations were performed with about 5×10^{-5} M solutions in 1×1 cm^2 quartz cells. The solutions were degassed on a high-vacuum line, using the freeze-pump-thaw technique, and sealed off.

Solvents. Methylcyclohexane and isopentane (Fluka purum) were chromatographed.[16] Acetonitrile and ethanol (Uvasol Merck) were used without further purification.

Spectra. UV spectra were recorded on a Perkin-Elmer Model 320 recording spectrophotometer. Mass spectra were measured on a Varian MAT Model CH 7 instrument at 70 eV and NMR spectra on a Bruker WH 270 pulse Fourier transform (270 MHz) instrument.

Flash Photolysis. The flash apparatus has been described elsewhere.[4c] The cooling technique of Fischer[18] was applied for experiments at low temperatures. The optical path length of the flash cells was 100 mm.

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Registry No. **1**-MAN, 34160-17-3; **2**-EAND, 83160-30-9; **2**-AN, 135-88-6; **2**-MAN, 6364-05-2; **2**-MANS, 64032-78-6; **7**-EBCD, 83160-31-0; **7**-BC, 205-25-4; **7**-MBC, 29103-83-1; **7**-MBCS, 83160-32-1; **9**, 54903-06-9; **10**, 83160-33-2; **11**, 83160-34-3; **15**, 83160-35-4; **16**, 5425-53-6; *N*-acetyl-2-naphthylamine, 581-97-5; bromobenzene-d_5, 4165-57-5.

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Torsional Potential Function of *n*-Butane. Correlation Effects in the Quantum-Mechanical Prediction of the Syn-Anti Energy Difference

F. A. Van-Catledge*[1a] and N. L. Allinger*[1b]

Contribution from the Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19898, and the Department of Chemistry, University of Georgia, Athens, Georgia 30602. *Received December 21, 1981*

Abstract: Hartree-Fock-Roothaan (HFR) calculations have been carried out by using a split-valence (6-31G) basis set for the title conformations of *n*-butane. The calculated energy difference was 6.36 kcal/mol, compared to 5.99 kcal/mol reported earlier for an STO-3G basis set. (Both calculations used molecular mechanics (MM2) optimized geometries for which the energy difference is 4.73 kcal/mol.) Inclusion of polarization functions at the HFR level leaves the energy difference virtually unchanged, 6.48 kcal/mol. Configuration interaction calculations over 11 665 of 33 234 possible singly and doubly excited valence configurations reduce the energy difference to 4.58 kcal/mol.

The *n*-butane molecule is a fundamental unit, an understanding of which is required for conformational analysis of hydrocarbons. There are four important torsional extrema: 0° (syn or cis), ~60° (gauche), ~120° (eclipsed), and 180° (anti or trans). While the latter three conformations are reasonably well understood, the syn form has presented some difficulties.[2] Theoretical estimates of the syn-anti energy difference have been derived on several occasions from Hartree-Fock-Roothaan (HFR) calculations,[3] but no *direct* experimental values are available (vide infra). The most reliable (in our judgement) HFR value for this difference is 5.99 kcal/mol (STO-3G),[2] but this is significantly higher than the molecular mechanics value of 4.73 kcal/mol (MM2).[4] We do not see how the HFR value could be utilized in molecular mechanics to give reasonable results. We, therefore, concluded earlier[2] that the HFR value must be in error by ~1 kcal/mol. Such an error might be ascribed to basis set limitations, but the STO-3G basis set has seemed to be adequate for hydrocarbons in the past.[2]

Inclusion of electron correlation effects will give a lower calculated energy than the HFR formalism for a given molecule and choice of basis set. It is expected,[5] and generally found, that the energy lowering is similar for different conformations of the same molecule. It has been suggested, however, that this discrepancy between the MM2 and HFR values is due to correlation effects.[2] The near-constancy of correlation effects is a necessary condition for the validity of HFR conformational studies. This is usually assumed to hold for "simple" alkanes. Even so, recent studies of 1,2-difluoroethene have demonstrated the importance of correlation effects in accounting for the cis-trans energy difference.[6] There is reason to believe that a similar effect is operative for the syn and anti forms of *n*-butane. In the former conformation the methyl groups approach each other quite closely, well within their van der Waals radii. Their is substantial van der Waals repulsion, but masked by this is a van der Waals attraction previously estimated to be about 1 kcal/mol.[2] This dispersion energy is essentially a correlation effect, accommodated within the molecular

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