Spectral and photochemical properties of bifunctional compounds and their complexes

2.* Photocyclization of α,ω-bis(diphenylamino)alkanes to α,ω-di(carbazolyl)alkanes

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Quantum yields of the step-by-step photocyclization of diphenylamine (DPA) derivatives $Ph_2N-(CH_2)_n-NPh_2$, $n = 3-6, 9$, to the corresponding α,ω-di(carbazolyl)alkanes were measured. At $n > 3$, the presence of the second DPA group had no effect on the cyclization of the first DPA group; however, cyclization of the second DPA group was retarded after cyclization of the first DPA group. The effect was explained by quenching of the excited DPA group by the carbazole group newly formed in the semi-cyclic compound. For disubstituted propane ($n = 3$), the mutual influence of the two groups at both stages of the reaction was found.

Key words: bifunctional compounds, diphenylamine, photocyclization, carbazole, energy transfer.

We have previously[1] shown that the interaction of two diphenylamine groups in α,ω-bis(diphenylamino)alkanes $Ph_2N-(CH_2)_n-NPh_2$ (**1**) is manifested in the electronic spectrum only for diamine with $n = 3$ in the form of changing the relative intensity of two absorption bands; at $n > 3$ the spectra of all diamines are similar and correspond to the doubled spectrum of *N*-alkylated diphenylamine.

The interaction of functional groups can substantially affect not only the spectral properties but also the direction and rate of photochemical reactions of bifunctional compounds.[2,3] Intramolecular cyclization to carbazole is a characteristic photochemical reaction of diphenylamine (DPA). The study of the reaction mechanism showed[4—8] that cyclization occurs in the excited triplet state followed by the oxidation of intermediate dihydrocarbazole to carbazole by oxygen.

In this work, we studied the specific features of the photochemical behavior of α,ω-bis(diphenylamino)alkanes $Ph_2N-(CH_2)_n-NPh_2$ (**1a—e**), where $n = 3$ (**a**), 4 (**b**), 5 (**c**), 6 (**d**), and 9 (**e**). It was shown that during irradiation both diphenylamine groups in diaminoalkanes successively enter cyclization to carbazole groups, and α-diphenylamino-ω-carbazolylalkanes **2** are the intermediate products of photocyclization, whereas the corresponding α,ω-di(carbazolyl)alkanes **3** are the final products. It was found that the quantum yield of cyclization of the first group is much higher than that of the second group. Analysis of the position of levels of singlet- and triplet-excited diphenylamine and carbazole explained the retardation effect observed for the photocyclization of the diphenylamine group in the presence of the carbazole group by the energy transfer from the excited first group to the second group.

Experimental

Diaminoalkanes **1**, aminocarbazolylalkanes **2**, and dicarbazolylalkanes **3** were synthesized by alkylation of DPA or carbazole by the corresponding mono- and dibromo- or diiodoalkanes according to the previously described procedures.[9,10—11]

Absorption spectra were recorded on a Specord M-40 spectrophotometer in quartz cells with the optical path length $l = 10$ mm. The accuracy of determination of wavelengths was 100 cm^{-1}. The concentrations of reagents were varied within $10^{-5}-10^{-4}$ mol L^{-1}. Acetonitrile ("for liquid chromatography" trade mark) was used as a solvent.

Irradiation was carried out by a DRSh-500 lamp through UFS-2 and ZhS-3 light filters (313 nm). The flux power measured by a PP-1 cavity receiver was $(1-1.2) \cdot 10^{-3}$ W cm^{-2}, which corresponds to $(2.6-3.1) \cdot 10^{-6}$ Einstein dm^{-3} s^{-1} for our experimental conditions and $\lambda = 313$ nm. All experiments were carried out at room temperature in air-saturated samples.

Results and Discussion

As seen in Fig. 1, during the reaction two absorption bands of the *N*-alkylated diphenylamine group at 250 and 300 nm disappear, and the characteristic absorption

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* For Part 1, see Ref. 1.

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 8, pp. 1510—1515, August, 1999.

1066-5285/99/4808-1491 $22.00

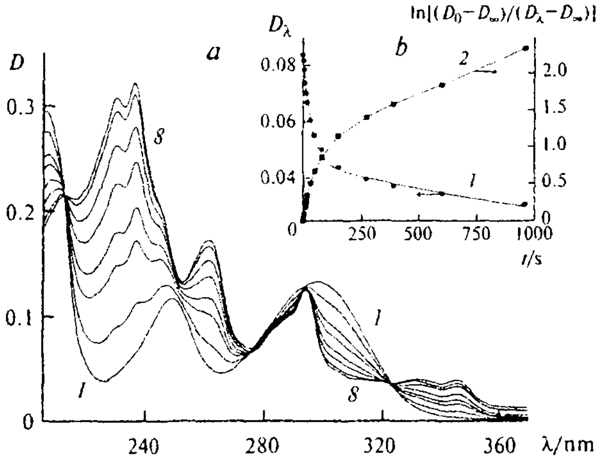


Fig. 1. *a*. Spectral changes during irradiation of a solution of **1b** ($5.08 \cdot 10^{-6}$ mol L^{-1}) in acetonitrile at irradiation time: 0 (*1*), 10 (*2*), 30 (*3*), 50 (*4*), 120 (*5*), 270 (*6*), 600 (*7*), and 960 s (*8*); light intensity is $3.04 \cdot 10^{-6}$ Einstein dm^{-3} s^{-1}. *b*. Kinetics of changing the optical density at the wavelength λ = 313 nm: *1*, experimental points and theoretical curve calculated by numerical integration of Eq. (2); *2*, anamorphosis of experimental data in coordinates of Eq. (1).

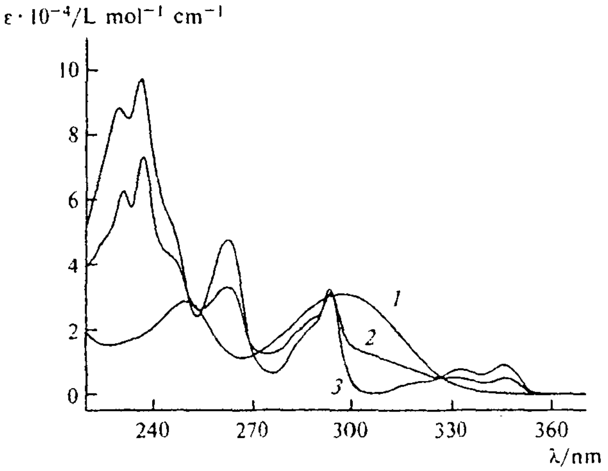
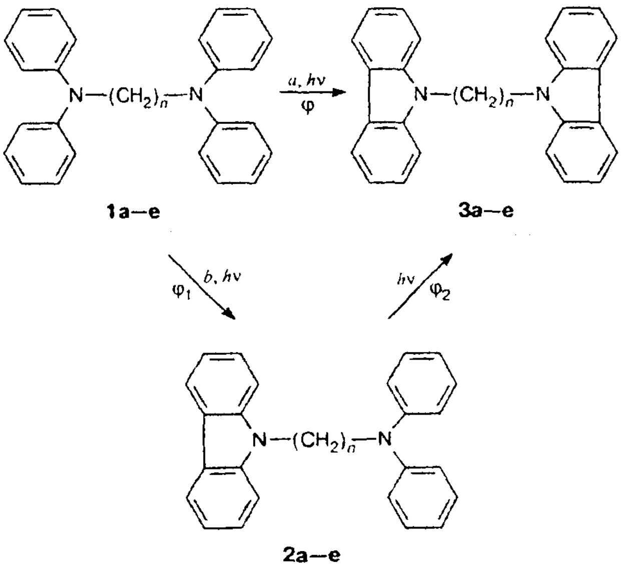


Fig. 2. Absorption spectra of diaminobutane **1b** (*1*), aminocarbozolylbutane **2b** (*2*), and dicarbazolylbutane **3b** (*3*) in acetonitrile.

bands of the carbazole ring with maxima at 229, 236, 262, 294, 332, and 346 nm appear, indicating the formation of the cyclization product. Similar spectral changes were also observed for other diaminoalkanes under study.

Two pathways of the reaction are possible in the case of diaminoalkanes **1** (Scheme 1): direct cyclization of two diphenylamino groups to carbazole groups with the quantum yield φ (*a*) and step-by-step cyclization with the intermediate formation of semi-cyclic aminocarbazolylalkane **2** with the quantum yield φ_1 followed by cyclization of the second diphenylamine group with the quantum yield φ_2 (*b*).

Scheme 1



The final products of photocyclization of diaminoalkanes **1**, dicarbazolylalkanes **3**, have been described in the literature, and the interaction of their functional groups is under intense study.[12—15] For **1b**, we also synthesized a possible intermediate cyclization product, aminocarbazolylbutane **2b**. It is seen in Fig. 2 that the spectrum of **2b** is, in fact, a half-sum of the spectra of **1b** and **3b**. Therefore, two pathways of the reaction cannot be distinguished from the analysis of spectral changes only, and the intermediate spectrum (*5*) in Fig. 1 can both belong to intermediate **2b** and be a superposition of the spectra of the initial (**1b**) and final (**3b**) cyclization products.

At the same time, depending on the reaction route (route *a* or *b*), the kinetic regularities of the process differ substantially. In the first case, the optical density of the reaction mixture (D_λ) at the time moment *t* is the sum of the optical densities of diamino- and dicarbazolylalkane, and at weak light absorption ($D_{313} < 0.1$), the kinetics of the D_λ change should obey the integral equation

$$\ln[(D_0 - D_\infty)/(D_\lambda - D_\infty)] = 2.3\varepsilon_{DA,313}\varphi I_0 t, \qquad (1)$$

where D_0 and D_∞ are the initial and final optical densities of the reaction mixture at the wavelength of observation λ, respectively; $\varepsilon_{DA,313}$ is the absorption coefficient of diaminoalkane (L mol cm^{-1}) at the wavelength of irradiation (313 nm); and I_0 is the incident light intensity (Einstein dm^{-3} s^{-1}).

Processing of the experimental data in coordinates of Eq. (1) showed (see Fig. 1, *b*) two distinct linear regions in which the slopes of the kinetic curve (*2*) differ substantially. TLC monitoring of the reaction course also indicated the two-stage mechanism *b*. In this case, the rates of changing the concentrations of diaminoalkane (C_{DA}), aminocarbazolylalkane (C_{AC}), and dicarbazolylalkane (C_{DC}) are described by the following system of equations:

$$dC_{DA}/dt = -\varphi_1(D_{DA,313}/D_{313})(1 - 10^{-D_{313}})I_0,$$

$$dC_{AC}/dt = [\varphi_1(D_{DA,313}/D_{313}) - \varphi_2(D_{AC,313}/D_{313})] \times \\ \times(1 - 10^{-D_{313}})I_0,$$

$$dC_{DC}/dt = \varphi_2(D_{AC,313}/D_{313})(1 - 10^{-D_{313}})I_0,$$

and the optical density of the reaction mixture is determined by the sum of three components

$$D_\lambda = (\varepsilon_{DA,\lambda}C_{DA} + \varepsilon_{AC,\lambda}C_{AC} + \varepsilon_{DC,\lambda}C_{DC})l,$$

where $\varepsilon_{\mathbf{X},\lambda}$ and $D_{\mathbf{X},\lambda}$ are the absorption coefficient and optical density, respectively, of substance **X** at the λ wavelength. From this we obtain the differential equation for the rate of changing the observed optical density

$$dD_\lambda/dt = [\varphi_1(\varepsilon_{AC,\lambda} - \varepsilon_{DA,\lambda})(D_{DA,313}/D_{313}) + \\ + \varphi_2(\varepsilon_{DC,\lambda} - \varepsilon_{AC,\lambda})(D_{AC,313}/D_{313})] \times \\ \times l(1 - 10^{-D_{313}})I_0. \quad (2)$$

Equation (2) cannot be solved in the analytical form. To verify that the experimental data correspond to this equation, we analyzed the dependence of the mean-square error of the optical density on the φ_1 and φ_2 parameters $\Delta D = [\Sigma(D_{calc} - D_\lambda)^2/m]^{1/2}$, where D_{calc} is the optical density calculated by numerical integration of Eq. (2), D_λ is the measured optical density, and *m* is the number of experimental points (Fig. 3). The quantum yields φ_1 and φ_2 were determined by minimization of the function $\Delta D(\varphi_1,\varphi_2)$ by the coordinate descending method and are presented in Table 1, and the theoretical curve that was calculated from the quantum yields and describes the experimental data is shown in Fig. 1, *b* (curve (*1*)).

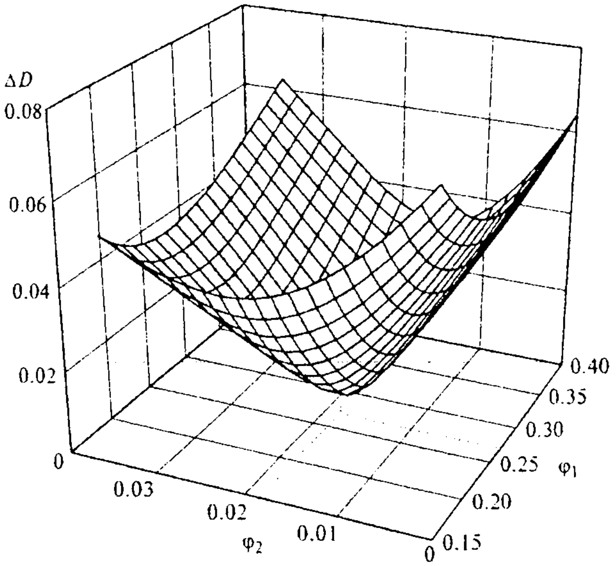


Fig. 3. Mean-square error of the calculated optical density $\Delta D = [\Sigma(D_{calc} - D_{exp})^2/m]^{1/2}$ (*m* is the number of experimental points) as a function of quantum yields φ_1 and φ_2 for compounds **1b**.

Table 1. Quantum yields of photocyclization of the first (φ_1) and second (φ_2) diphenylamine groups in diaminoalkanes **1** (air-saturated acetonitrile, 298 K)

Compound	φ_1	φ_2
1a	0.12±0.02	0.041±0.009
1b	0.27±0.03	0.017±0.003
1c	0.27±0.03	0.013±0.003
1d	0.27±0.03	0.019±0.004
1e	0.28±0.03	0.035±0.007

The calculated relative concentrations of three components of the reaction mixture during photolysis of a solution of **1b** are presented in Fig. 4. It is seen that at the moment *t* = 120 s, to which the intermediate spectrum (*5*) in Fig. 1 corresponds, the reaction mixture consists of aminocarbazolylalkane **2b** by ≥90 %.

Analysis of the data in Table 1 shows that for the length of the methylene bridge *n* > 3 the quantum yield φ_1 remains unchanged within the measurement error.

Therefore, the presence of the second diphenylamine group has almost no effect on the cyclization of the first group, which agrees with the previously made[1] (from the study of the spectral properties) conclusion about the absence of the interaction of functional groups in diaminoalkanes **1** at *n* > 3.

It is seen in Table 1 that for diaminoalkanes (*n* > 3) the values of quantum yields φ_2 are an order of magnitude lower than φ_1 and increase gradually with increase in the methylene chain length. Therefore, after cycliza-

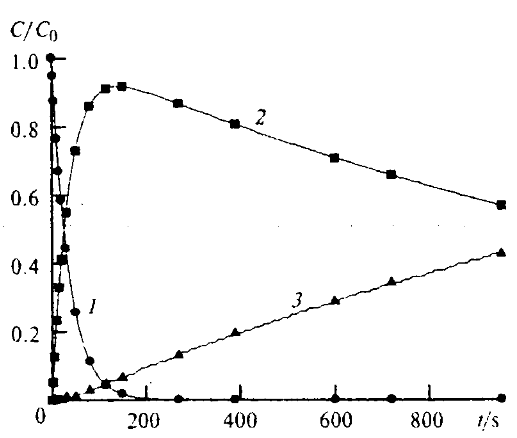


Fig. 4. Change in the relative concentrations of components during photolysis of diaminobutane **1b**: **1b** (*1*), **2b** (*2*), and **3b** (*3*). Experimental conditions correspond to those presented in Fig. 1 (C_0 = 5.08 · 10^{-6} mol L^{-1}).

tion of the first diphenylamine group, the cyclization of the second group is sharply retarded, *i.e.*, the carbazole group formed at the first stage acts as the quencher at the second stage of the photochemical reaction, and the influence of the carbazole group weakens with increase in distance between the groups.

The data obtained can be explained as follows. The singlet (S_1) and triplet (T_1) levels of DPA lie at 31100 and 25140 cm^{-1}, and those in the case of carbazole lie at 29500 and 24690 cm^{-1}, respectively,[16] *i.e.*, lower than the levels of DPA. Therefore, the carbazole group can be a quencher of both the singlet- and triplet-excited diphenylamine group. At the wavelength of irradiation (313 nm), the absorption coefficients of two chromophoric groups, diphenylamine and carbazole, are equal to 8170 and 790 L mol cm^{-1}, respectively. Comparison of these values shows that during irradiation of the intermediates of the reaction, aminocarbazolylalkanes **2**, the light is mainly absorbed by the diphenylamine group; however, due to the energy transfer, excitation is localized on the carbazole group, thus preventing cyclization of the diphenylamine group. Taking into account the published data,[15] the electron transfer can make some contribution to the quenching process.

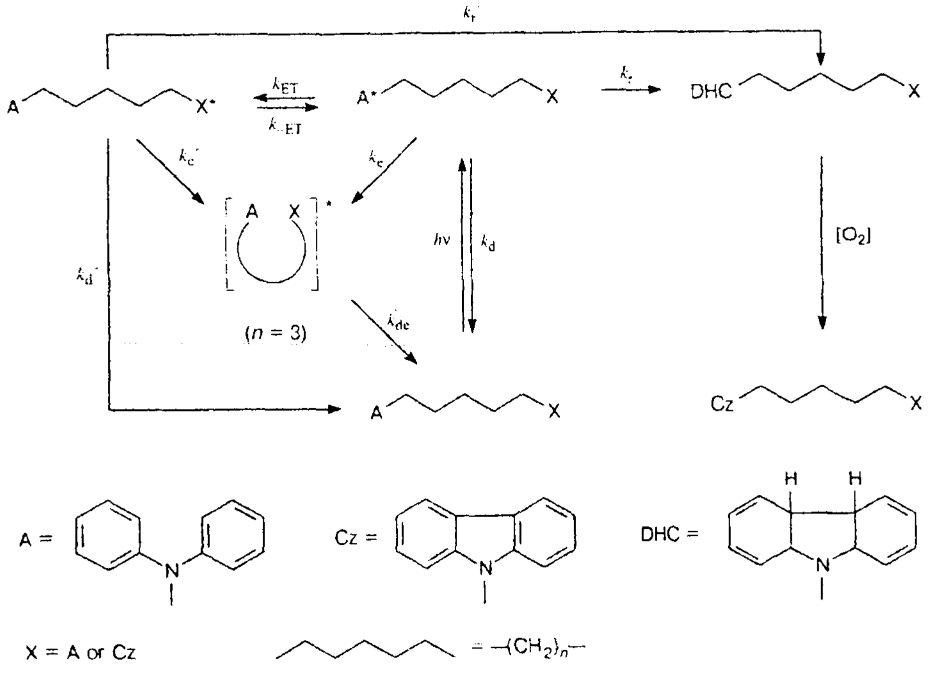
Let us consider the properties of diaminoalkane **1a** with the trimethylene bridge. Comparison of the φ_1 and φ_2 quantum yields for this amine with the data for other amines shows that the functional groups interact during the cyclization of both second and first diphenylamine groups. Taking into account the available data on the properties of 1,3-diphenyl-,[17] 1,3-dinaphthyl-,[18] 1,3-dipyrenyl-,[19] and 1,3-dicarbazolylpropane **3a**,[14,15] we should assume the formation of an intramolecular excimer in the excited state of diaminoalkane **1a**. In this case, this process competes with the chemical reaction and results in a decrease in the quantum yield φ_1.

A similar formation of the exciplex occurs, evidently, in excited aminocarbazolyl alkane **2a** as well. In addition, in this compound, due to a short distance between the chromophoric groups and a small value of the energy gap between the excited states of two groups (see above), a reverse transfer of the electron energy from carbazole to DPA is possible (*cf.* Ref. 20), which results in an increase in the probability of cyclization and, correspondingly, in an increase in the quantum yield φ_2.

The photochemical and photophysical processes under discussion that occur during excitation of bifunctional DPA derivatives can conveniently be presented by a generalized scheme (Scheme 2). For simplicity and due to the general character of the processes, direct and reverse energy transfer (k_{ET} and k_{-ET}), formation and deactivation of the excimer or exciplex (k_e, k_e', and k_{de}), and the singlet- and triplet-excited states are not distinguished in Scheme 2; however, it should be taken into account that the cyclization does not occur in the singlet-excited state for which k_r (k_r') $\ll$ k_d (k_d'). The k_d and k_d' constants summate all processes of nonradiative and radiative deactivation of local excited states, except for those indicated above. Conformers of bifunctional compounds, except "extended" and "folded" forms at n = 3 (exciplex formation), are not distinguished in Scheme 2.

At the first stage of the reaction, for excitation of diaminoalkane (in this case, X = A), k_{ET} = k_{-ET}, k_d =

Scheme 2



k_d', and $k_r = k_r'$. Therefore, for the parallel change in these parameters at $n > 3$, the φ_1 quantum yield is independent of n. At $n = 3$ an additional deactivation channel appears that is related to the formation of the excimer (since X = A, $k_e = k_e'$), which results in a decrease in φ_1 for **1a**.

At the second stage of the reaction, for excitation of aminocarbazolylalkane (X = Cz), $k_{ET} > k_{-ET}$, and $k_r' = 0$ (this reaction channel is absent). At $n > 3$, the φ_2 quantum yield is determined as $\varphi_2 = \varphi_t[k_r/(k_d + k_{ET} + k_r)]$, where φ_t is the quantum yield of the triplet-excited state (proportional to the intersystem crossing rate constant). The rate constant of triplet-triplet energy transfer is the following:

$$k_{ET,t} = \varphi_t k_r/\varphi_2 - (k_d + k_r) = \varphi_t k_r(1/\varphi_2 - 1/\varphi_0),$$

where $\varphi_0 = \varphi_t k_r/(k_d + k_r)$ is the quantum yield of cyclization in the absence of a quencher. Based on this equation, we can estimate the $k_{ET,t}$ values assuming that $\varphi_0 = 0.28$ (see Table 1) and φ_t remains unchanged (the absence of singlet-singlet energy transfer). Using the known parameters for *N*-methyldiphenylamine,[6] $\varphi_t = 0.89$ and the lifetime of the triplet-excited state of 13.6 ns, we find $k_r = 2.3 \cdot 10^7$ s^{-1} necessary for the calculation.

The obtained $k_{ET,t}$ values are presented in Fig. 5 (curve *1*) along with similar constants for other bichromophoric systems. Comparison shows that when two chromophoric groups are linked by a sufficiently rigid bridge (α,ω-disubstituted cyclohexane or *trans*-decalin, curve *2*), the transfer rate constant decreases rapidly with increase in the number of bridging atoms, because the transfer energy occurs through σ-bonds. For the systems with the flexible polymethylene bridge (curves *1*, *3*, and *4*), such as aminocarbazolylalkanes **2**, the transfer rate constant depends much more weakly on the number of bridging atoms, because the energy transfer through the space becomes a predominant mechanism, and the flexible bridge allows the molecule of the bichromophoric compound to accept conformations in which two chromophoric groups are brought together.

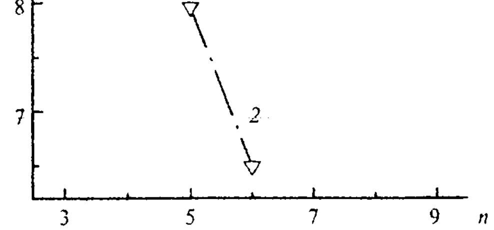


Fig. 5. Dependence of the rate constant of triplet-triplet energy transfer ($k_{ET,t}$) on the number of atoms (*n*) connecting the energy donor and acceptor: α-diphenylamino-ω-carbazolylalkanes **2** (*1*), α-(2-naphthyl)-ω-(4-benzophenoyl)cyclohexanes and *trans*-decalins[21] (*2*), cinnamyl esters of ω-benzoylalkane acids[22] (*3*), and ω-(4-*o*-toluylphenoxy)alkanophenones[20] (*4*).

Considering another limiting case, when the decrease in the quantum yield at the second stage of cyclization is related only to a decrease in the φ_t constant, we can estimate the rate constant of singlet-singlet energy transfer $k_{ET,s}$, which varies for compounds **2b—e** from $3.9 \cdot 10^9$ to $1.8 \cdot 10^9$ s^{-1}. The obtained $k_{ET,s}$ values lie within the corresponding parameters for α,ω-bis(2-naphthyl)-alkanes[23] (10^7—10^8 s^{-1}) and those for bichromophoric coumarins, in which two coumarin dyes are linked by the polymethylene chain,[24] 10^{11}—10^{12} s^{-1}.

Thus, both models, singlet-singlet and triplet-triplet energy transfer, make it possible to describe the observed decrease in the quantum yield at the second stage of cyclization of α,ω-bis(diphenylamino)alkanes and the dependence of φ_2 on the alkyl chain length.

Despite intense studies of the photocyclization of diphenylamine and its derivatives to carbazoles, the inhibition effects of the reaction products have not been described up to now. The special experiment showed[6] that the quantum yield of photocyclization of *N*-methyldiphenylamine is independent of the initial concentration of amine when the latter increases to $3 \cdot 10^{-3}$ mol L^{-1}. Taking into account that the lifetime of this compound in the triplet-excited state is equal[6] to 13.6 ns and assuming a diffusionally controlled limit for the quenching constant (~10^{10} L mol^{-1} s^{-1}), we find that the concentration of the quencher should be ≥0.01 mol L^{-1}. This value is much higher than those commonly used in experiments on cyclization of amines with concentrations of 10^{-5}—10^{-3} mol L^{-1} and corresponds to the concentrations of additives in experiments on quenching. The same calculation explains why photocyclization occurs efficiently in air. As known, dioxygen is a quencher of triplet-excited states; however, its concentration in air-saturated organic solvents is ~10^{-3} mol L^{-1}, which is insufficient to exert an effect on photocyclization. By contrast, in this case, dioxygen plays a positive role, oxidizing intermediate unstable dihydrocarbazole to carbazole (see Scheme 2).

The authors thank V. B. Nazarov for help in photolysis experiments and M. M. Kantor for the program for computer processing of experimental data.

The work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32342).

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Received January 9, 1998;
in revised form April 10, 1998