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Self-quenching in the stepwise photocyclization of 1,4-bis(diphenylamino)butane to 1,4-dicarbazolylbutane

Mikhail F. Budyka,* Olga D. Laukhina and Tatyana N. Gavrishova

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588; e-mail: budyka@icp.ac.ru

The quantum yields of stepwise cyclization of the first and second diphenylamino groups in 1,4-bis(diphenylamino)butane are 0.3 and 0.02, respectively, which indicates quenching of the excited diphenylamino group by a carbazole unit in the asymmetric semi-cyclized compound.

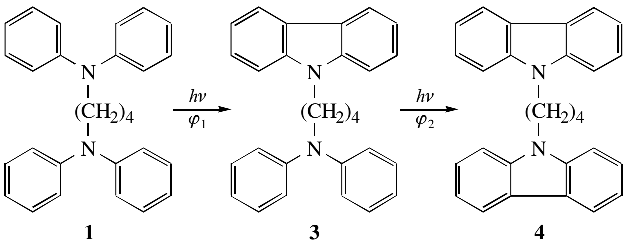
On irradiation, diphenylamine and derivatives are known to form the corresponding carbazoles by an intramolecular cyclization reaction.[1–5] The cyclization has been shown to proceed in the excited triplet state followed by oxidation of intermediate dihydrocarbazole to carbazole by oxygen.

In this communication we report the peculiarities of the photocyclization of the bichromophoric derivative of diphenylamine, namely, 1,4-bis(diphenylamino)butane **1**. The photochemical properties of the model compounds, *N*-butyldiphenylamine **2** and 1-(*N*-diphenylamino)-4-(*N*-carbazolyl)butane **3** are also considered for comparison.

An air-saturated acetonitrile solution of **1** (5.08×10^{-6} M) was irradiated at 313 nm (light intensity 3×10^{-6} einstein dm^{-3} s^{-1}). Spectrum (*1*) in Figure 1 belongs to pure **1**, whereas the final spectrum (*7*) coincides with the spectrum of 1,4-dicarbazolylbutane **4**. This compound was identified by its characteristic absorption ($\lambda_{\rm abs}$ ~ 240, 260, 290 and 340 nm) and fluorescence ($\lambda_{\rm fl}$ ~ 350 and 365 nm) spectra and by comparison (thin layer chromatography) with a thermally synthesized sample. Therefore, **4** is the final product of the photocyclization of **1**.

Aminocarbazole **3**, which is a semi-cyclized compound with a diphenylamino group on one side of the methylene bridge and a carbazole group on the other, is a possible intermediate in the diamine cyclization reaction. The model asymmetric compound **3** was synthesized. The absorption spectrum of **3** was proved to be the half-sum of the spectra of **1** and **4**, and to coincide with spectrum (*4*) in Figure 1.

Investigation of the kinetics of photocyclization (see insert in Figure 1) shows clearly that the reaction proceeds in two stages, with a fast first stage, spectra (*1*) → (*4*), and a slow second stage, spectra (*4*) → (*7*). Based on this fact, and on the coincidence between the intermediate spectrum (*4*) in Figure 1 and the absorption spectrum of aminocarbazole **3**, the following two-step scheme for the photochemical reactions can be proposed (Scheme 1).



Scheme 1

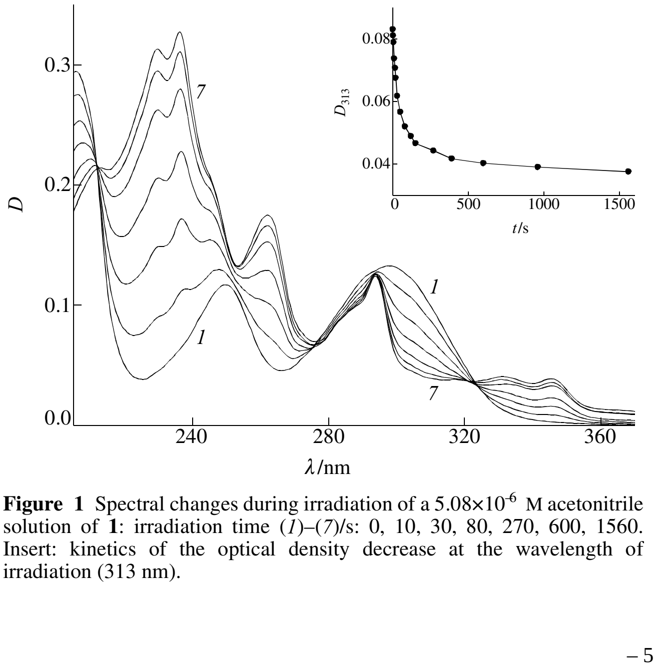


Figure 1 Spectral changes during irradiation of a 5.08×10^{-6} M acetonitrile solution of **1**: irradiation time (*1*)–(*7*)/s: 0, 10, 30, 80, 270, 600, 1560. Insert: kinetics of the optical density decrease at the wavelength of irradiation (313 nm).

The rate of photochemical transformation of substance X is expressed by equation (1):

$$d[X]/dt = -\varphi_X (D_X/D)(1 - 10^{-D}) I_0 \quad (1)$$

where φ_X and D_X are, respectively, the quantum yield of the reaction and optical density of the substance X at the irradiation wavelength, D is the optical density of the reaction mixture at the same wavelength and I_0 is the intensity of incident light (einstein dm^{-3} s^{-1}).

In the case of a thin optical layer ($D < 0.1$) and monitoring the reaction kinetics at the irradiation wavelength, equation (1) can be integrated and gives for time t:

$$\ln[(D_t - D_\infty)/(D_0 - D_\infty)] = -2.3\varepsilon_X \varphi_X l I_0 t \quad (2)$$

where ε_X is the absorption coefficient (M^{-1} cm^{-1}) of X at the irradiation wavelength and l is the optical path (cm).

In addition to diamine photocyclization, reaction kinetics of the model compounds **2** and **3** were investigated. All kinetic data are treated in terms of equation (2) and are compared in Figure 2.

One can see that, firstly, the kinetics of diamine photocyclization, curve (*1*), in the initial stage of the reaction are similar to those of the monoamine photocyclization, straight

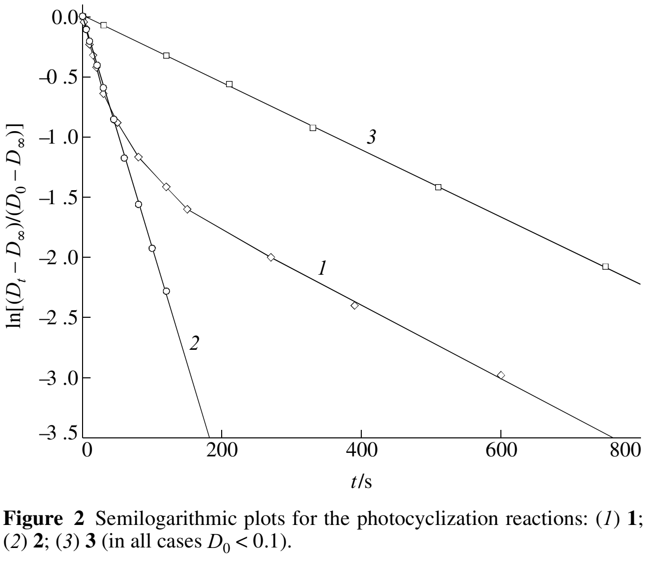


Figure 2 Semilogarithmic plots for the photocyclization reactions: (*1*) **1**; (*2*) **2**; (*3*) **3** (in all cases $D_0 < 0.1$).

line (*2*), whereas the kinetics of the final stage of the diamine reaction are similar to those of the aminocarbazole photocyclization, straight line (*3*); and, secondly, the slopes of both lines differ markedly. The quantum yields for the first (φ_1) and the second (φ_2) diphenylamino groups cyclization in **1** are calculated to be 0.3 and 0.02, respectively.

Thus, an investigation of the photocyclization reaction of diamine **1** in comparison with reactions of the model monoamine **2** and aminocarbazole **3** shows that the presence of the second diphenylamino group has no effect on the photocyclization of the first diphenylamino group, whereas the photocyclization of the second diphenylamino group is retarded after the photocyclization of the first diphenylamino group. Therefore, the carbazole group is a quencher for the photocyclization reaction of the diphenylamino group in semicyclized compound **3**.

Symmetrically , -disubstituted alkanes have attracted many researchers in connection with an investigation of the problem of functional group interaction.[6–11] In the case of alkanes with carbazole[6] and diphenylamino[11] groups no intramolecular interaction of functional groups was observed, provided the number of linking CH_2 groups exceeded 3 (number of linking -bonds exceeded 4). In this respect, the properties of bifunctional compounds with flexible polymethylene chains differ markedly from those with rigid polynorbornyl bridges, where interaction has been observed through up to 6 -bonds.[12]

The absence of any diphenylamino group interaction in **1**[11] agrees with our finding that the quantum yield of the first diphenylamino group photocyclization in **1** ($\varphi_1 = 0.3$) is equal to that of monoamine **2** photocyclization. However, the small value of $\varphi_2 = 0.02$ points to the stronger interaction of the two functional groups in asymmetrically disubstituted butane **3** compared to symmetrically substituted butanes **1** and **4**.

The data obtained can be explained as follows. Singlet (S_1) and triplet (T_1) levels of diphenylamine lie at 31100 and 25140 cm^{-1}, and those of carbazole lie at 29500 and 24690 cm^{-1}, respectively.[13] The interchromophoric edge-to-edge distance in **3** does not exceed 5.1 Å and in such compounds the energy transfer proceeds on a time scale of several picoseconds for the singlet-singlet transfer[14] and of tens of nanoseconds for the triplet-triplet one.[15] Taking into account the lifetimes of the lowest excited states of the diphenylamine chromophore, *i.e.* 4.0×10^{-9} s for the singlet and 2.7×10^{-5} s for the triplet state,[16] one should expect effective quenching of both singlet and triplet excited diphenylamine groups by a carbazole group. So, on irradiation of **3** the excitation appears to be localised at the carbazole group thus preventing cyclization of the diphenylamino group. The possibility of quenching by an electron transfer mechanism should not be neglected either.

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