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Photochemical reaction of *trans*-di(α-naphthyl)ethylene with diphenylamine

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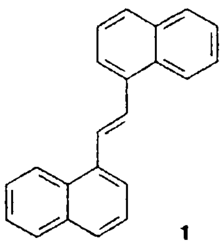
Diphenylamine adds to the ethylene bond of excited *trans*-di(α-naphthyl)ethylene (**1**). Dependence of the quantum yields of mono- and bi-molecular reactions of **1**, *cis*-di(α-naphthyl)ethylene **2**, and dihydropicene **3** on amine concentration was studied. On this basis and theoretical analysis of the kinetic scheme a conclusion was drawn that amine interacts with excited **1** with a diffusion-limited rate but has no effect on the photochemical activity of **2** and **3**. The reaction mechanism was discussed.

Key words: diarylethylene, diphenylamine, photoisomerization, photocyclization, photoaddition.

Photochemical properties of the "diarylethylene—amine" system are under intense study.[1—5] Depending on the nature of amine and solvent polarity, photoirradiation of diarylethylenes in the presence of amines can result in the formation of a luminescent exciplex or adducts with different structures.

trans-Di(α-naphthyl)ethylene (**1**) is a convenient object for studying photoinduced reactions, because, unlike many diarylethylenes,[6] the photochemical behavior of **1** is not impeded by the presence of several conformers in the solution. It has recently been shown[7] that diphenylamine has a substantial effect on the photochemical properties of **1**. The results were interpreted in terms of the common two-stage scheme[8,9] "isomerization—cyclization," according to which **1** is first photoisomerized to *cis*-isomer **2** and the latter further undergoes photocyclization to dihydropicene (**3**).



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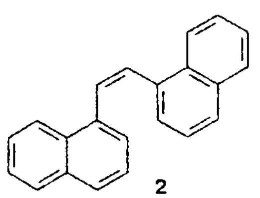

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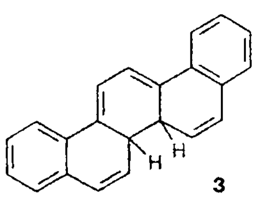

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However, further study of the photochemical properties of **1** showed[10] the adiabatic channel of direct cyclization of **1** to **3** without intermediate formation of **2**. This route of the reaction has not previously been considered.[7] In addition, chemical reactions between diphenylamine and compound **1** have been reported,[7] but the nature of the reactions has not been studied.

In this connection, we studied in detail the photochemical reactions in the *trans*-di(α-naphthyl)ethylene—diphenylamine system.

Experimental

A DRSh-500 mercury lamp was used as the radiation source. The spectral line at 365 nm was picked out by a set of UFS-6 and BS-7 light filters, and the line of 446 nm was picked out by ZhS-11 and SS-15 filters.

If necessary, the solutions were degassed by multiple freezing—evacuation to 0.02 Torr—thawing out.

For preparative photolysis, a degassed solution of the *trans*-isomer (21.6 mg, 0.026 mol) and diphenylamine (99.6 mg, 0.196 mol) in toluene (3 mL) was irradiated for 13 h at λ = 365 nm by light with an intensity of $5 \cdot 10^{-6}$ Einstein dm^{-3} s^{-1}. The solvent was removed *in vacuo*, and the residue was recrystallized from EtOH. The product was finally purified from the diphenylamine residue by column chromatography (Silpearl as packing, hexane as the eluent). Yellowish crystals of the product (6 mg) with m.p. 105—106 °C were obtained. ^{1}H NMR (CDCl$_3$), δ: 3.74—3.88 (m, 1 H, CH$_2$); 4.00—4.14 (m, 1 H, CH$_2$); 5.15—5.21 (m, 1 H, CH); 5.63 (s, 1 H, NH); 6.71—8.10 (m, 23 H, H arom.). According to HPLC data, the reaction mixture also contains an insignificant amount of picene and other compounds, presumably, the isomeric products of addition of diphenylamine to **1**.

For kinetic experiments, we used solutions of compounds **1** ((1—2) $\cdot$ 10^{-5} mol L^{-1}), **2** ((4—7) $\cdot$ 10^{-5} mol L^{-1}), and di-

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phenylamine (with a variable concentration) in toluene. Irradiation was carried out by light with a wavelength of 365 nm and an intensity of (1.4—1.7) $\cdot$ 10^{-6} Einstein dm^{-3} s^{-1}, and then by light with a wavelength of 446 nm and an intensity of (3.2—3.6) $\cdot$ 10^{-6} Einstein dm^{-3} s^{-1} (measured by a PP-1 cavity receptor). All experiments were carried out at room temperature in a quartz cell with an optical path length l = 10 mm.

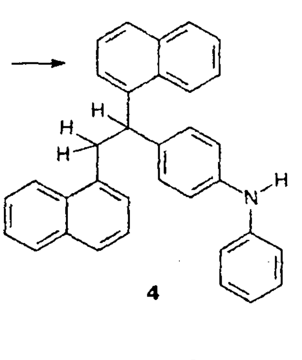
Electronic absorption spectra were recorded on a Specord M-40 instrument; IR spectra were recorded on a Specord M-82 spectrophotometer; ^{1}H NMR spectra were obtained on a Bruker AM-300 instrument; and mass spectra were obtained on a Kratos MS-890 instrument at an ionizing electron energy of 70 eV and temperature of the ionization chamber of 150 °C; the intensities of peaks are presented relative to the maximum peak.

Results and Discussion

Structure of adduct

According to the mass spectrometric data, the mass of the molecular ion $[M]^+$ of the main product of the photochemical reaction of diphenylamine with compound **1** is 449 (7%), which corresponds to the addition of an amine molecule (the mass $[M]^+$ is equal to 169) to dinaphthylethylene ($[M]^+$ = 280). Addition at the ethylene bond is the standard direction of the photochemical reaction of amines with diarylethylenes.[4,5] In the case of diphenylamine, both C-adduct **4** and N-adduct **5** can be formed. In this case, C-adduct **4** is formed; the IR spectrum in the region of 3400 cm^{-1} (KBr) contains bands of vibrations of the amino group, and the ^{1}H NMR spectrum exhibits a singlet of the proton of the amino group at 5.63 ppm.

1 + Ph_2NH $\xrightarrow{h\nu}$



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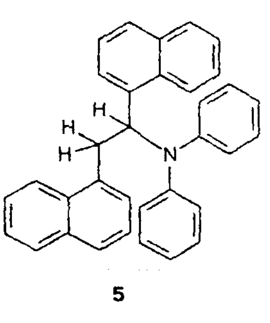

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Dissociation of the central C—C bond is the most characteristic route for decomposition of adduct **4** under electron impact (similar to di(α-naphthyl)ethane[11]). The charge is mainly localized on the fragment containing the amino group (m/z = 308), and the intensity of the peak of this ion is maximum in the spectrum; the intensity of the peak of the second fragment with m/z = 141 is 44%.

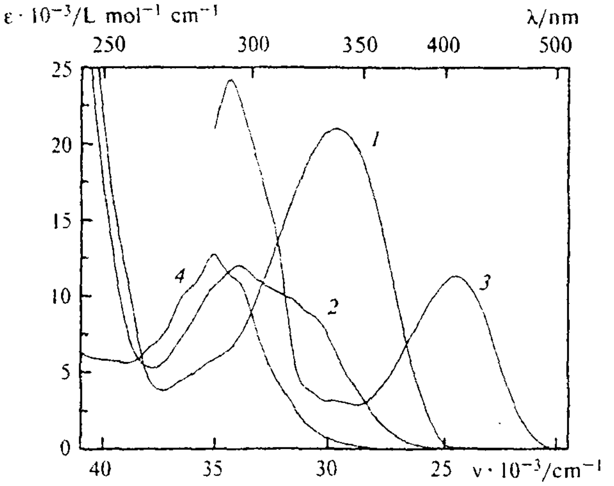


Fig. 1. Absorption spectra in EtOH; numeration of the spectra corresponds to numbers of compounds.

The structure of adduct **4** is also consistent with the UV spectroscopic data. The observed sharp shift of the maximum of the absorption band to the short-wave region (as compared to the spectrum of initial dinaphthylethylene **1**) (Fig. 1, spectra *4* and *1*, respectively) corresponds to the cleavage of the conjugation chain between two naphthyl rings during addition at the ethylene bond in compound **4**.

Despite a substantial difference in experimental conditions (the solution and the solid matrix), our data correlate with the results of studying photoadditions in a polycrystalline mixture of diphenylamine and stilbene.[5] It has been shown[5] that the reaction proceeds *via* two directions: to form adducts with C—N and C—C bonds, the latter always predominating, and in the case of threefold excess of diphenylamine, the reaction affords nothing but the C—C adducts. In our case, under the conditions of preparative photolysis, the diphenylamine excess was 7.5, and in kinetic studies, it was varied within 10^3—10^4. It is most likely that the addition of amine to **1** occurs through a similar mechanism (see below) regardless of the matrix (the solution or the solid matrix).

Reaction kinetics

According to the published data,[10] at least five successive-parallel photochemical reactions (Scheme 1, reactions φ_1—φ_5) proceed in the system under study in the absence of amine. In the presence of diphenylamine, they should be supplemented by the addition of the latter to *trans*-isomer **1** (φ_6). As mentioned,[10] it is convenient to monitor the change in the concentration of dihydropicene **3** at λ = 410 nm, where the other components of the mixture do not absorb (see Fig. 1, ε_3 = 13000 L mol^{-1} cm^{-1}). At the irradiation wavelength of 365 nm, absorption coefficients are the following: ε_1 = 12470 L mol^{-1} cm^{-1}, ε_2 = 1120 L mol^{-1} cm^{-1}, and

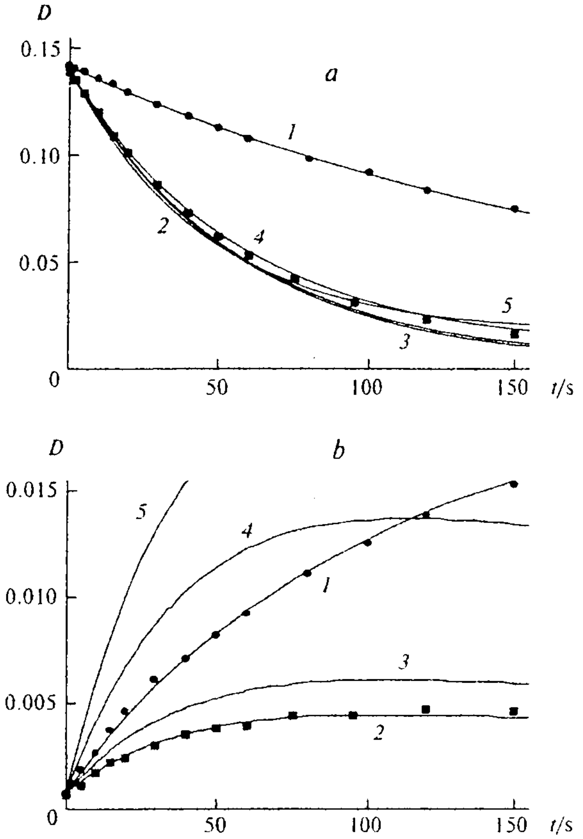
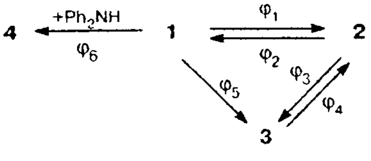


Fig. 2. Kinetics of changes in the optical density at wavelengths of 365 nm (*a*) and 410 nm (*b*) during irradiation of a solution of *trans*-isomer **1** ($1.12 \cdot 10^{-5}$ mol L^{-1}): experimental points and theoretical curves in the absence (*1*) and presence of 0.1 *M* diphenylamine (*2—5*). Theoretical curves were calculated from Eqs. (1)—(5) and data in Table 1 at the ratio of constants k_4/k_5 = 100 (*2*), 10 (*3*), 1 (*4*), and 0.1 (*5*).

ε_3 = 4960 L mol^{-1} cm^{-1}. Comparison of the kinetic curves recorded at 365 and 410 nm shows that in the presence of amine, the rate of consumption of **1** increases (Fig. 2, *a*, curves *1* and *2*), and the rate of formation of dihydropicene **3** decreases (Fig. 2, *b*, curves *1* and *2*).

Scheme 1



Diphenylamine does not absorb at λ > 350 nm (λ_{max} = 284 nm). When amine is added, the spectrum of **1** at λ > 350 nm remains unchanged, *i.e.*, these compounds do not form complexes in the ground state. Thus, irradiation with light at λ = 365 nm results in the initial moment in selective excitation of only *trans*-isomer **1**, and in the further course of the reaction, compounds **2** and **3** that formed are also excited.

It turned out that the reaction of *cis*-isomer **1** with diphenylamine at the same exposure did not result in the formation of adduct **4**, and only cyclization and isomerization are observed. Therefore, the direct reaction **2** + Ph_2NH → **4** is absent from Scheme 1. When the *cis*-isomer is irradiated for a long time, adduct **4** is formed from the *trans*-isomer that appeared in the reaction (φ_2). However, since the φ_2 value is low and $\varphi_2 \ll \varphi_1$ (see Ref. 10), the concentration of the *trans*-isomer is insignificant, and this route is inefficient.

According to Scheme 1, the change in concentrations of the reagents during irradiation of the reaction mixture is described by the following system of differential equations (irradiation with light at 365 nm):

$$d[\mathbf{1}]/dt = [-(\varphi_1 + \varphi_5 + \varphi_6)(D_{1,365}/D_{365}) + \\ + \varphi_2(D_{2,365}/D_{365})](1 - 10^{-D_{365}})I_0, \tag{1}$$

$$d[\mathbf{2}]/dt = [\varphi_1(D_{1,365}/D_{365}) - (\varphi_2 + \varphi_3)(D_{2,365}/D_{365}) + \\ + \varphi_4(D_{3,365}/D_{365})](1 - 10^{-D_{365}})I_0, \tag{2}$$

$$d[\mathbf{3}]/dt = [\varphi_3(D_{2,365}/D_{365}) - \varphi_4(D_{3,365}/D_{365}) + \\ + \varphi_5(D_{1,365}/D_{365})](1 - 10^{-D_{365}})I_0, \tag{3}$$

$$d[\mathbf{4}]/dt = \varphi_6(D_{1,365}/D_{365})(1 - 10^{-D_{365}})I_0, \tag{4}$$

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

$$D_\lambda = (\varepsilon_{1,\lambda}[\mathbf{1}] + \varepsilon_{2,\lambda}[\mathbf{2}] + \varepsilon_{3,\lambda}[\mathbf{3}] + \varepsilon_{4,\lambda}[\mathbf{4}])l, \tag{5}$$

where $\varepsilon_{X,\lambda}$ and $D_{X,\lambda}$ are the absorption coefficient and optical density of compounds **X** at the λ wavelength, respectively; and I_0 is the light intensity (Einstein dm^{-3} s^{-1}).

The system of equations (1)—(4) with account for equation (5) in the general form has no analytical solution and should be solved numerically.[12] However, in the case of the reaction of **1** with diphenylamine, search for the solution is difficult because adduct **4** does not absorb at λ > 350 nm (see Fig. 1, spectrum *4*). In addition, absolute values of some parameters have no substantial effect on the final result of the calculation. For example, the change in ΔD upon variation of the quantum yields φ_3 and φ_4 for *trans*-isomer **1** and specified values of other parameters is shown in Fig. 3. A broad "valley" is observed on the surface $\Delta D = f(\varphi_3,\varphi_4)$, due to which φ_3 and φ_4 may vary within wide limits without affecting the calculation error, and only the φ_3/φ_4 ratio is important. This can be explained by the previously found[10] ratio of quantum yields: φ_3, $\varphi_4 > \varphi_1$, φ_5. According to this, the rate of accumulation of compounds **2** and **3** is determined by slow isomerization (φ_1)

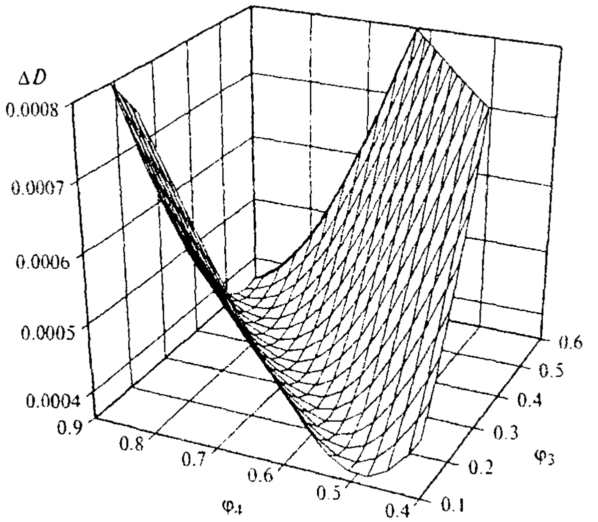


Fig. 3. Influence of changes in φ_3 and φ_4 on the mean-square error of the optical density ($\Delta D = [\Sigma(D_{\rm calc} - D_{\rm exp})^2/m]^{1/2}$) when *trans*-isomer **1** is used as the initial reagent.

and cyclization (φ_5), whereas equilibrium between **2** and **3** is rapidly established and depends only on the φ_3/φ_4 ratio and the corresponding absorption coefficients.

By contrast, this ratio plays a positive role in the description of reaction of *cis*-isomer **2**. Due to this, compounds **2** and **3** are the main components of the mixture in the initial region of the reaction. Therefore, only terms containing concentrations and optical densities of these compounds are significant in Eqs. (1)—(5). Numerical solution of the system of equations gives the quantum yields $\varphi_3 = 0.55 \pm 0.05$ and $\varphi_4 = 0.8 \pm 0.1$, which agrees with the published data.[10] These values remain unchanged within the error regardless of the presence of dioxygen and amine within the concentration interval of the latter to 0.1 mol L^{-1}.

The φ_4 value was also obtained independently in special experiments. At first, when *cis*-isomer **2** was irradiated with light at λ = 365 nm, dihydropicene **3** accumulated in the solution, and then it was selectively excited with light at λ = 436 nm. This resulted in only reaction **3** → **2** with the quantum yield $\varphi_4 = 0.8 \pm 0.1$, which is independent of the presence of amine (to concentrations of 0.1 mol L^{-1}) and dioxygen (in the interval of λ = 365—436 nm, and the reaction is also independent of the wavelength of irradiation).

When *trans*-isomer **1** is used as the initial compound, in the initial time moment ($t \to 0$) we have $[\mathbf{2}] \approx [\mathbf{3}] \approx [\mathbf{4}] \approx 0$; hence, from Eqs. (1) and (5) we obtain

$$dD_\lambda/dt = -\varphi\, \varepsilon_{1,\lambda}\, l(1 - 10^{-D_{365}})I_0,$$

where $\varphi = \varphi_1 + \varphi_5 + \varphi_6$. All processes involving the excited *trans*-isomer are presented in Scheme 2. Here the k_1 constant characterizes monomolecular radiative and nonradiative processes of deactivation of **1***, except for isomerization and cyclization, which are summated by the k_2 constant; the k_3 constant is assigned to physical quenching of **1*** by amine, k_4 characterizes the addition of amine to **1***, and k_5 refers to the sum of amine-sensitized isomerization and cyclization.

Scheme 2

$$\mathbf{1}^* \xrightarrow{k_1} \mathbf{1}$$

$$\mathbf{1}^* \xrightarrow{k_2} \mathbf{2} + \mathbf{3}$$

$$\mathbf{1}^* + \mathrm{Ph_2NH} \xrightarrow{k_3} \mathbf{1} + \mathrm{Ph_2NH}$$

$$\mathbf{1}^* + \mathrm{Ph_2NH} \xrightarrow{k_4} \mathbf{4}$$

$$\mathbf{1}^* + \mathrm{Ph_2NH} \xrightarrow{k_5} \mathbf{2} + \mathbf{3} + \mathrm{Ph_2NH}$$

According to Scheme 2, the quantum yield of consumption of **1** is determined as

$$\varphi = \frac{k_2 + (k_4 + k_5)[\mathrm{Ph_2NH}]}{k_1 + k_2 + (k_3 + k_4 + k_5)[\mathrm{Ph_2NH}]},$$

from which we obtain

$$\varphi/(1 - \varphi) = \{k_2 + (k_4 + k_5)[\mathrm{Ph_2NH}]\}/(k_1 + k_3[\mathrm{Ph_2NH}]). \quad (6)$$

The quantum yields of consumption of **1** were determined from the initial regions of the kinetic curves of the dependence of D_{365} on t. It follows from the linear dependence (r = 0.999) of the $\varphi/(1 - \varphi)$ ratio on the amine concentration (Fig. 4) that $k_1 >> k_3[\mathrm{Ph_2NH}]$, *i.e.*, the physical quenching of the excited *trans*-isomer

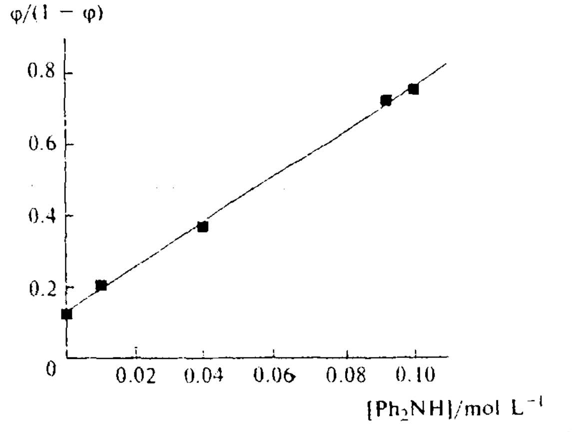


Fig. 4. Ratio $\varphi/(1 - \varphi)$ as a function of the concentration of diphenylamine (φ is the quantum yield of consumption of *trans*-isomer **1**, r = 0.999).

Table 1. Influence of the ratio of rate constants k_4/k_5 on the quantum yields of consumption of **1** at a concentration of diphenylamine of 0.1 mol L^{-1}

k_4/k_5	φ_1	φ_5	φ_6
0.1	0.299	0.099	0.032
1	0.191	0.063	0.176
10	0.082	0.028	0.32
100	0.06	0.02	0.35

Note. $\varphi = \varphi_1 + \varphi_5 + \varphi_6 = 0.43$.

by amine can be neglected. The straight line in Fig. 4 is described by the equation

$$\varphi/(1 - \varphi) = 0.13 + 6.33[Ph_2NH].$$

Comparison of this equation with Eq. (6) gives $k_2/k_1 = 0.13$ and $(k_4 + k_5)/k_1 = 6.33$. Since $k_2/k_1 + 1 = 1/k_1\tau_0$ (τ_0 is the lifetime of excited compound **1**), we obtain $(k_4 + k_5)\tau_0 = 6.33/1.13 = 5.6$ L mol^{-1}. Taking into account that the lifetime of the singlet excited state of **1** is equal[13] to 2 ns, we find the rate constant of chemical quenching of **1** by diphenylamine, $k_q = k_4 + k_5 = 2.8 \cdot 10^9$ L mol^{-1} s^{-1} close to the rate constant of the diffusion-limited reaction in toluene.

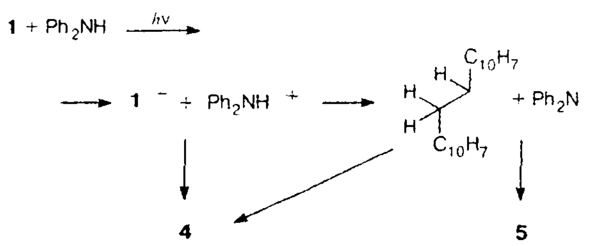
Each of the k_2 and k_5 constants summates the rate constants of two reactions of the *trans*-isomer, isomerization, and cyclization. It is reasonable to assume that in the presence of amine, the previously found[10] ratio $\varphi_1/\varphi_5 = 3$ remains unchanged (the latter is determined by the shape of the potential energy surface of the excited state[14]). Then we can calculate the contribution of each of the parameters to the total φ value at different ratios of constants k_4/k_5 (Table 1). The values obtained were used for calculation of the theoretical kinetic curves from Eqs. (1)—(4) taking into account Eq. (5).

It is seen in Fig. 2, *a* that the curves calculated for $\lambda = 365$ nm (the optical density of the *trans*-isomer makes the main contribution to them) are poorly sensitive, especially in the initial region, to the value of each term, but change substantially when the total quantum yield φ increases from 0.11 (curve *1*) to 0.43 (curves *2*—*5*). At the same time, analysis of the kinetic curves of accumulation of dihydropicene (410 nm, Fig. 2, *b*) favors the relationship of the constants $k_4 \gg k_5$. Therefore, the reaction with amine rather than isomerization and cyclization is the main channel of consumption of *trans*-isomer **1** in the presence of diphenylamine.

Reaction mechanism

It is usually assumed that during photoaddition of both aliphatic[4] and aromatic[5] amines to diarylethylenes, a proton is transferred from the amine radical cation to the diarylethylene radical anion after photoelectron transfer, and then the recombination of two neutral radicals occurs (Scheme 3).

Scheme 3



However, when aromatic amines are used as donors, recombination at the stage of radical ion products involving C atoms of benzene rings of amine is also possible. Taking into account the unpaired electron density in the diphenylamine radical cation,[15] the attack of radical anion $1^{\cdot -}$ on C atoms in the *para*-position to the N atom of the radical cation with the formation of the C-adduct can be considered the main direction of the reaction in this case. The formation of the N-adduct (along with the C-adduct) is possible only after deprotonation of the radical cation during recombination with the participation of the neutral amine radical, because attack at the N atom is shielded in the radical cation.[15]

It is clear from the scheme considered that the factors stabilizing the radical ion pair and decreasing the yield of neutral radicals, for example, an increase in the medium polarity, favor the recombination of radical ions resulting in an increase in the relative content of the C-adduct. It is this effect that has been observed[5] on going from a mixture of diphenylamine and stilbene to their acetonitrile solutions. In the reaction of diphenylamine with compound **1**, steric hindrances due to repulsion of naphthyl rings of **1** and phenyl rings of amine are an additional factor that prevents the formation of adduct **5**.

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