# ON THE MECHANISM OF THE EFFECT OF AROMATIC AMINES ON THE FLUORESCENCE AND PHOTOCHEMICAL OXIDATION OF ANTHRACENE COMPOUNDS

Table 1

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## Abstract

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# ON THE MECHANISM OF THE EFFECT OF AROMATIC AMINES ON THE FLUORESCENCE AND PHOTOCHEMICAL OXIDATION OF ANTHRACENE COMPOUNDS

*(Presented by Academician A. N. Terenin, May 7, 1962)*

In order to further study the mechanism of the effect of fluorescence quenchers on the quantum yields of fluorescence and photosensitization of anthracene compounds [1–3], the fluorescence-quenching constants of several anthracene compounds by a whole series of aromatic and aliphatic amines were determined, as well as the changes, under the influence of these amines, in the quantum yield of photosensitization ($\Phi_\phi$) of 9,10-di-*n*-propylanthracene (Table 1).

**Table 1**

Values of the bimolecular fluorescence-quenching constants ($K_T$), the relative constants of interaction of the quencher with the intermediate photooxide ($m_2/k_3$) of 9,10-di-*n*-propylanthracene, dissociation constants ($K_a$), and ionization potentials of a series of organic amines

| Quenchers | 9,10-di-*n*-propylanthracene (10.4)* | 9-methoxymethylanthracene (3.5) | 9-hydroxymethylanthracene (5.1) | 9-chloroanthracene (4.3) | 9-bromoanthracene (2.4) | 9,10-dichloroanthracene (7.3) | $K_a \cdot 10^{10}$ in $H_2O$ at 25° [13–15] | Ionization potentials in vapors, eV | $m_2/k_3$ |
|---|---|---|---|---|---|---|---|---|---|
| *N*, *N*-Dimethylaniline | 7.2 | 8.0 | 11.7 | 12.2 | 12.6 | 12.5 | 11.5 | $7.4 \pm 0.03$ [12] | – 7.34 [13] |
| *N*, *N*-Dimethyl-*p*-toluidine | 5.8 | 9.2 | 10.1 | 10.7 | 10.0 | 11.9 | – | 7.06 [15] | 920 |
| *p*-Toluidine | 3.7 | 5.7 | 7.9 | 8.8 | 8.0 | 10.6 | 11.8 | – | 203 |
| *o*-Toluidine | 3.6 | 4.5 | 7.3 | 8.0 | 8.3 | 11.0 | 2.47 | – | – |

| Quenchers | 9,10-di-*n*-propylanthracene (18.4)* | 9-methoxymethylanthracene (3.5) | 9-hydroxymethylanthracene (5.1) | 9-chloroanthracene (4.3) | 9,10-dichloroanthracene (2.4) | 9-cyanoanthracene (7.3) | $K_a \cdot 10^{10}$ in $H_2O$ at 25° (13–15) | Ionization potentials in vapors, eV | $m_2/k_3$ |
|---|---|---|---|---|---|---|---|---|---|
| Aniline | 2.8 | 4.5 | 6.2 | 7.7 | 7.7 | 9.2 | 3.82 | 7.69± 0.02[12] | 47 7.64[13] 7.55[13] |
| *N*, *N*-Dimethyl-*o*-toluidine | 2.7 | 3.8 | 7.2 | 7.9 | 6.4 | 9.3 | – | – | 130 |
| *m*-Chloroaniline | 0.39 | – | 3.4 | 5.4 | – | 7.3 | – | – | – |
| Triphenylamine | 0.65 | – | 6.7 | – | – | – | – | – | – |
| Benzylamine | 0.2 | – | – | 0 | – | 0 | $2.4 \cdot 10^5$ | 8.64± 0.02[12] | 0.4 |
| Dimethylamine | 0 | 0 | – | 0 | – | 0 | $5.2 \cdot 10^6$ | 8.24[14] | 30 |
| Diethylamine | 0 | – | – | 0 | – | – | $9.6 \cdot 10^6$ | – | – |
| Amine salts | 0 | 0 | – | 0 | – | 0 | – | – | – |

* In parentheses are the values of the lifetimes of the excited state of the corresponding compounds in air and in the absence of quenchers, $\tau \cdot 10^9$ sec.

All measurements were carried out with alcoholic solutions.* The bimolecular quenching constants were calculated from the formula following from the expression for the quantum yield of fluorescence in the presence of a quencher (scheme in [1]):

$$K_T = (B/B_T - 1) : [T] \cdot \tau,$$

where $B$ and $B_T$ are the quantum yields of fluorescence in air in the absence and in the presence of a quencher,** $[T]$ is the quencher concentration, and $\tau$ is the lifetime of the excited state in air in the absence of a quencher. The values of $B_T$ were determined for several concentrations of the quencher, and the data obtained were averaged graphically (Fig. 1). The values of $B$ were taken from work [5] for all substances except 9,10-di-*n*-propylanthracene, for which–

* The method for measuring the quantum yields of fluorescence and photosensitization is described in [4]. The fluorescence spectra of the anthracene compounds studied do not change in the presence of the quenchers used.

Figure 1 graph: dependencies of the reciprocal fluorescence quantum yield on quencher concentration

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** In all the anthracene compounds studied, concentration quenching is either absent or does not manifest itself at the concentrations used.

of which $B = 0.60$. The values of $\tau$, averaged over several measurements on a phase fluorometer, are given in Table 1.

To elucidate the mechanism of fluorescence quenching in the cases studied, the quenching constants were first compared with the most characteristic and general property of amines—their proton-acceptor ability, expressed by the dissociation constants of organic bases in water, $K_a$*. This comparison shows (Table 1) that there is no relationship between the proton-acceptor and quenching properties of the amines studied. On the other hand, from the character of the change in the quenching constants by aromatic amines when their structure is varied, a definite regularity follows: toluidines and NH-dimethylated amines quench the fluorescence of anthracene compounds more strongly, whereas *m*-chloroaniline does so more weakly, than aniline. Such a sequence in the increase of $K_T$ values corresponds to an increase in the electron density on the benzene ring of the quencher. As

**Fig. 1.** Dependences of the reciprocal value of the fluorescence quantum yield of alcoholic solutions of anthracene compounds ($10^{-3}$ mol/l) on the concentration of quenchers ([T]):
1—9-chloroanthracene and aniline, 2—9-methoxyanthracene and NN-dimethyl-*p*-toluidine, 3—9-methoxyanthracene and NN-dimethylaniline, 4—anthracene and aniline, 5—9-methoxyanthracene and aniline, 6—9,10-dichloroanthracene and aniline, 7—9,10-dichloroanthracene and *m*-chloroaniline, 8—9,10-di-*n*-propylanthracene and NN-dimethylaniline, 9—9,10-di-*n*-propylanthracene and NN-dimethyl-*p*-toluidine, 10—9,10-di-*n*-propylanthracene and aniline

is known, the presence of an amino group as a substituent in the benzene ring increases the electron density on the latter through displacement of the free electron pair of the nitrogen atom toward the ring, i.e., the amino group belongs to electron-donor substituents. The methyl radical also belongs to this same type of substituent. Therefore, in toluidine and *N*-methylated aromatic amines the electron density on the benzene ring should be still greater than in aniline. Conversely, electron-acceptor substituents, for example chlorine, decrease the electron density on the ring. NN-dimethyl-*o*-toluidine does not fit into this regularity: it quenches fluorescence in the same way as aniline or even more weakly. But this agrees with the known fact that the *o*-methyl substituent brings the NN-dimethylamino group out of the plane of the benzene ring, which should hinder its conjugation with the ring ([7]). The fact that NN-dimethylaniline proves

to be a more effective quencher than NN-dimethyl-*p*-toluidine can probably be explained by the greater bulkiness of the latter, which may affect the approach of the excited molecule to the quencher molecule required for quenching. Salts of aromatic amines (for example, aniline hydrochloride), in which the free electron pair of nitrogen is bound by a proton, are not quenchers. The fluorescence intensity of a solution of 9,10-di-*n*-propylanthracene ($1.5 \cdot 10^{-3}$ mol/l),

* From the data of work ([6]) it may be concluded that, on going from water to alcohol, the relative ratio of $K_a$ values for different organic amines is preserved.

quenched by *p*-toluidine ($10^{-2}$ mole/liter) by more than a factor of 4, is completely restored at a hydrochloric-acid concentration of $10^{-2}$ mole/liter in the solution, and at a monochloroacetic-acid concentration of 1 mole/liter.

These observations lead to the conclusion that the primary act in the cases of fluorescence quenching under consideration may be electron transfer from the quencher to the excited molecule of the anthracene compound. Such a mechanism is also supported by data available in the literature on the ionization potentials of some of the amines used in the present work: for dimethylamine and benzylamine the ionization potentials are much

**Fig. 2.** Dependence of the quantum yield of photooxidation of 9,10-di-*n*-propylanthracene in an alcohol solution ($1.5 \cdot 10^{-3}$ mole/liter) in air on the amine concentration:
1 —diphenylamine (the point lying off the curve was obtained in an oxygen-free medium), 2 —dimethylamine, 3 —aniline, 4 —*o*-toluidine, 5 —NN-dimethyl-*o*-toluidine, 6 —*p*-toluidine, 7 —NN-dimethyl-*p*-toluidine. Dashed curves —dependences of the quantum yields of photooxidation on the quencher concentration, calculated on the assumption of their proportionality to the fluorescence quantum yields.

higher than for aromatic amines, and among the latter the highest value is that of aniline (but these values refer to vapors; in solutions, where solvation effects play a role, their magnitudes may be somewhat different).

The mechanism of electron transfer in reversible quenching of the fluorescence of complex aromatic molecules was proposed by Bauer ([8]) and then developed by Weiss ([9]), who assumed that the electron passes from the reducing quencher to a vacant position of the ground state of the excited molecule*. Direct experimental confirmation of the possibility of such electronic transitions is contained in the work of Leonard and Weller ([11]).

If the quenching mechanism has been correctly established for the examples considered, then a change in the electron density on the anthracene nucleus should affect the value of the quenching constant by a given quencher. Indeed, the data of Table 1 show that the fluorescence of substances containing electron-donor substituents (9-methylanthracene; 9-methoxyanthracene; 9,10-di-*n*-propylanthracene) is quenched less strongly than the fluorescence of anthracene, while the fluorescence of substances with an electron-acceptor sub-

stituent (mesochloro derivatives) is quenched more strongly. The latter, however, is very clearly manifested only in the example of 9,10-dichloroanthracene. As for the especially low values of the fluorescence-quenching constants of 9,10-di-*n*-propylanthracene, steric hindrance may play a role here because of the relative bulkiness of its molecules.

The mechanism of the influence of various amines on the photochemical oxidation of anthracene compounds was investigated using 9,10-di-*n*-propylanthracene as an example. All these compounds, like *p*-toluidine, suppress photooxidation strongly—

* A detailed discussion of Weiss' s theory is given in A. N. Terenin' s monograph ([10]), p. 252.

less than fluorescence (Fig. 2).* To characterize the interaction of amines with the intermediate photooxide, the values of the relative constants $m_2/k_3$ (1) were determined ($m_2$ is the rate constant of the interaction of the intermediate photooxide with quencher molecules, leading to regeneration of the initial anthracene compound; $k_3$ is the rate constant of spontaneous decomposition of the intermediate photooxide). If, in the ratio of the expressions for the fluorescence quantum yield in the presence of a quencher ($B_\mathrm{T}$) and for the quantum yield of photooxidation under the same conditions ($\varphi_{\phi\mathrm{T}}$(3)), one substitutes the numerical values of the constants (3) and the concentrations of oxygen ($1.34{\cdot}10^{-3}$ mol/l) and 9,10-di-*n*-propylanthracene ($1.5 \cdot 10^{-3}$ mol/l), the expression obtained is

$$B_\mathrm{T}/\varphi_{\phi\mathrm{T}} = 11.5 + 10 \cdot \frac{m_2}{k_3}[T],$$

where $10 \cdot \frac{m_2}{k_3}$ is the tangent of the angle of inclination of the straight line representing the dependence of the ratio $B_\mathrm{T}/\varphi_{\phi\mathrm{T}}$ on the quencher concentration to the axis of quencher concentrations (Fig. 3), whence $m_2/k_3 = (B_\mathrm{T}/\varphi_{\phi\mathrm{T}} - B_\mathrm{T}/\varphi_\phi)/10[T]$ ($B$ and $\varphi_\phi$ are the yields of fluorescence and photooxidation in the absence of quencher). From the obtained values of $m_2/k_3$ (Table 1) it follows that the increase in the inhibiting action of amines on photooxidation generally proceeds in parallel with the increase in the quenching constants. This confirms the conclusion that amines reduce the intermediate photooxide. As the first stage of the process, electron transfer apparently occurs here as well. Dimethylamine, which is not a quencher, also hinders photooxidation, i.e., it is also capable of reducing the intermediate photooxide.

**Fig. 3.** Dependence of the ratio of the fluorescence quantum yield ($B$) to the photooxidation quantum yield ($\varphi_\phi$) of 9,10-di-*n*-propylanthracene ($1.5 \cdot 10^{-3}$ mol/l) in alcoholic solutions in air on the concentration of quenchers: 1 —NN-dimethyl-*p*-toluidine, 2 —*p*-toluidine, 3 —NN-dimethyl-*o*-toluidine, 4 —aniline, 5 —dimethylamine, 6 —benzylamine.

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* Two of the quenchers studied behave otherwise. Diphenylamine reacts photochemically with 9,10-di-*n*-propylanthracene, disrupting the anthracene structure, since, despite quenching of fluorescence ($K_T$ = 4.3), the quantum yield of the photochemical transformation of the latter increases, and more strongly in an oxygen-free medium than in air (Fig. 2). The influence of *n*-phenylenediamine on the quantum yield of photooxidation could not be determined, because the products of its photochemical transformation absorb in the absorption region of 9,10-di-*n*-propylanthracene.

*Note: Figure translations are in progress. See original paper for figures.*