ELECTRON-TRANSFER AND COMPLEX FORMATION IN THE EXCITED STATE

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FLUORESCENCE†

Some years ago, while investigating fluorescence quenching of aromatic hydrocarbons (A) by typical electron donors (D), like anilines, we observed[1] a broad structureless emission band about 5000 cm^{-1} to the red of the fluorescence of the aromatic hydrocarbon of normal structure. This anomalous fluorescence, as shown in *Figure 1*, increases in intensity with increasing donor concentration at the expense of the fluorescence intensity of the hydrocarbon, thereby following the same Stern–Volmer-type relation as does the well known excimer fluorescence, e.g. in the case of pyrene[2]. Extrapolation to infinite donor concentration gives the dashed spectrum (cf. *Figure 1*) which
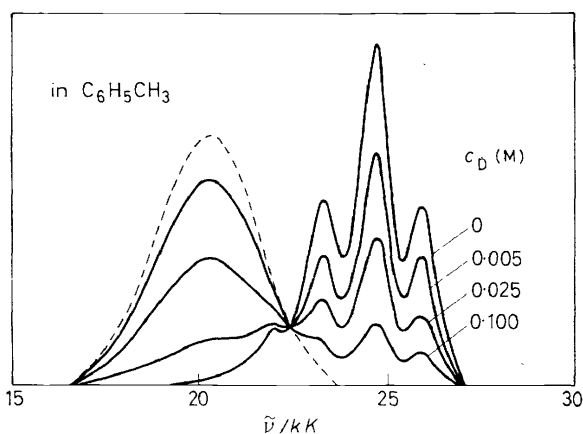

Figure 1. Fluorescence spectra of anthracene (3·4 × 10^{-5} M) in toluene at different concentrations, c_D, of diethylaniline

we ascribe to a charge-transfer complex formed in the excited state according to Eq. (1). *Figure 2* shows the absorption and fluorescence spectra of anthra-

$$^{1*}A + D \rightarrow {}^{1}(A^-D^+) \tag{1}$$

cene in toluene and diethylaniline as solvents. It is quite clear that there is no corresponding change in absorption accompanying the change in fluorescence.

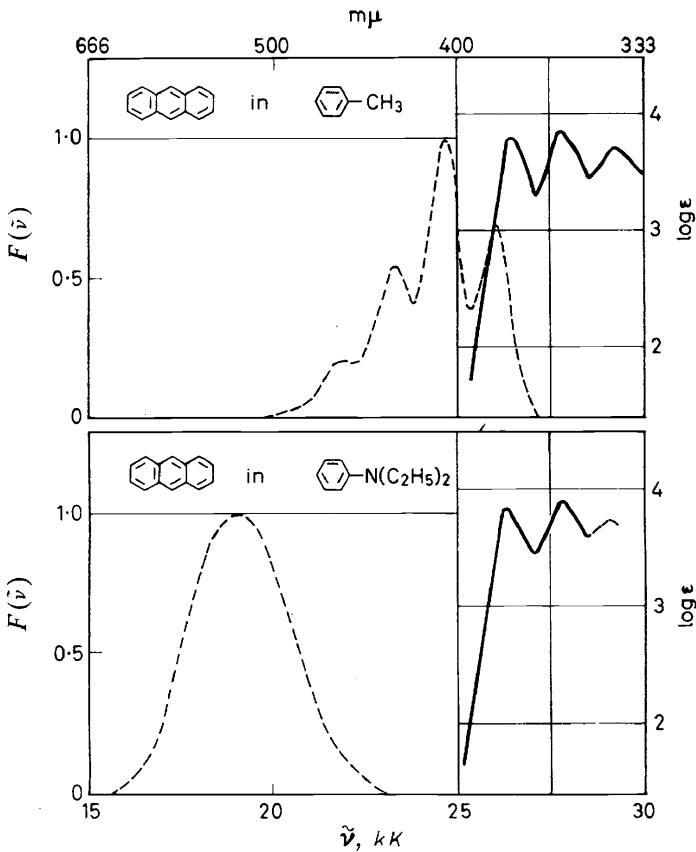† This work was carried out in collaboration with H. KNIBBE

Figure 2. Absorption and fluorescence spectra of anthracene in toluene (top) and diethyl-aniline (bottom)

When using an aromatic hydrocarbon such as biphenyl, which absorbs at shorter wavelengths than dialkylaniline, we obtained the fluorescence spectra given in *Figure 3*. Here, with increasing hydrocarbon concentration, c_A, the diethylaniline fluorescence is quenched and a new emission appears at longer wavelengths which, again, is ascribed to an excited charge-transfer complex. In this case the reaction is expressed by Eq. (2). These findings can

$$^{1*}D + A \rightarrow {}^1(D^+A^-) \tag{2}$$

be rationalized in terms of a very simplified molecular orbital scheme (cf. *Figure 4*). It is based on the idea that, in the complex, an electron has been transferred from the donor to the acceptor. Identifying the energy of the highest bonding orbital in either molecule with the ionization potential and that of the lowest antibonding orbital with the electron affinity one obtains the conditions which, apparently, must be fulfilled for this type of complex formation and emission to occur[3]. These conditions simply imply that it is always the molecule with the lower ionization potential which acts
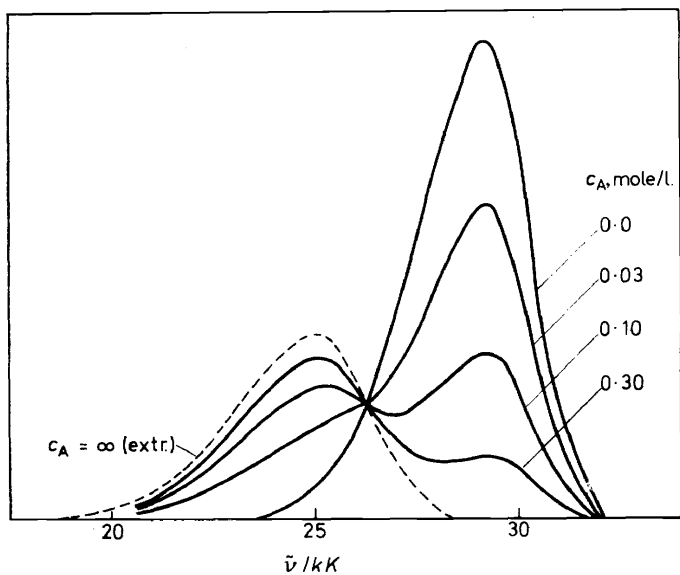
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Figure 3. Fluorescence spectra of diethylaniline (0·01 M) in toluene at different concentrations, c_A, of biphenyl
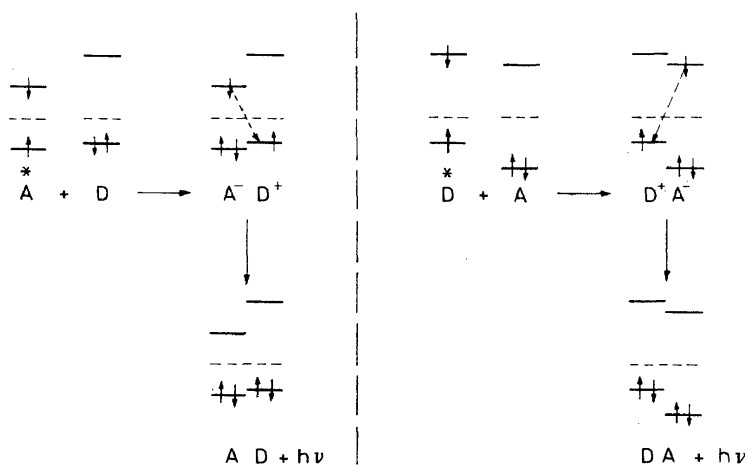

Figure 4. Molecular orbital scheme for interpretation of the complex emission

as donor and the one with the higher electron affinity which acts as acceptor.

A study of the influence of solvent on the complex fluorescence has revealed two effects whose interpretation adds considerably to the understanding of the mechanism of electron transfer reactions in solution. *Figure 5* shows the fluorescence spectra of the system: anthracene + diethylaniline in different solvents, whose dielectric constant (ϵ) increases from hexane (1·89) to acetonitrile (37). In all solvents the anthracene concentration was 5×10^{-4} M, whereas the diethylaniline concentration was chosen equal

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to the half-value quencher concentration, c_h, so that either of the fluorescence components had just half the intensity that it would have in the extreme cases of zero or infinite donor concentration, respectively. Two effects of increasing dielectric constant on the charge-transfer emission can be noticed: a red shift and a considerable decrease in intensity.
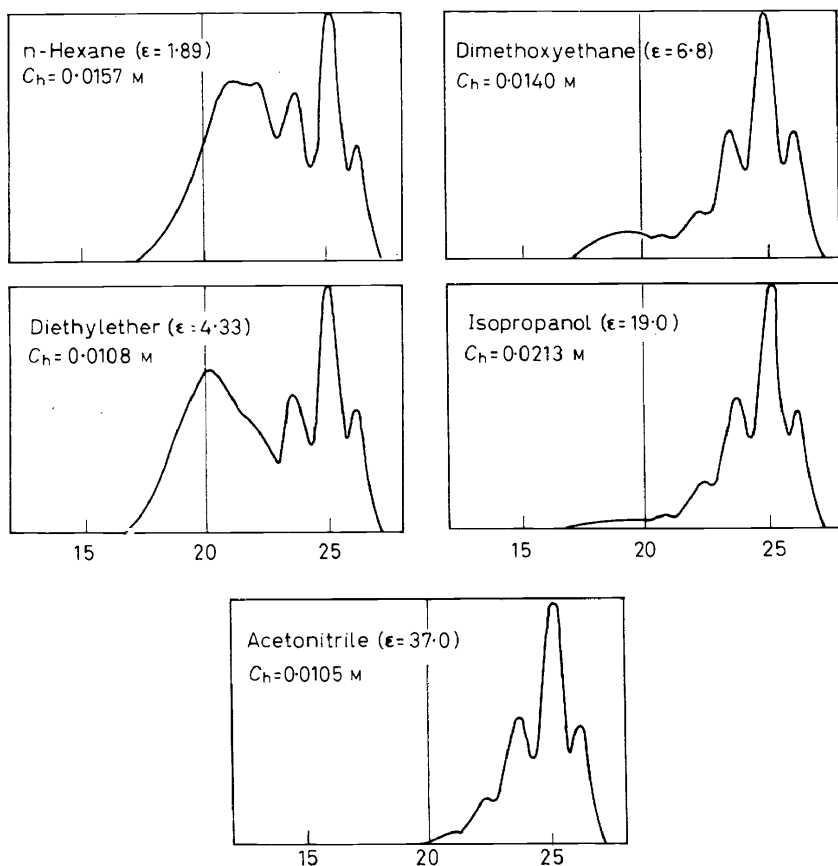

Figure 5. Fluorescence spectra of anthracene (5×10^{-4} M) + diethylaniline in different solvents; diethylaniline concentration equals the half-value quencher concentration, c_h (see text)

The solvent dependent red shift can easily be understood on account of the dipolar nature of the excited complex whose energy should decrease as the solvating property of the solvent increases. The complex fluorescence spectra of numerous A,D-combinations, measured in solvents of different polarity, have been evaluated[4] with the aid of Eq. (3) which can be derived from

$$\tilde{\nu}_{ct} = \tilde{\nu}_{ct}(0) - \frac{2\mu_{ct}^2}{hca^3}\left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2} \times \frac{n^2 - 1}{2n^2 + 1}\right), \qquad (3)$$

formulae given in the literature[5,6], by plotting the band maximum wave number $\tilde{\nu}_{ct}$, of the charge-transfer complex emission against the expression

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in parentheses (where n = index of refraction). Values obtained for μ_{ct}, the dipole moment of the excited complex, (assuming an equivalent radius of the complex volume, $a = 5$ Å) ranged from 10 Debye for the anthracene–diethylaniline complex to 13·5 Debye for the biphenyl–diethylaniline complex. These values, indeed, are indicative of predominant charge-transfer interaction in the excited complex. Recently, by the same procedure, μ-values below 7 Debye have been obtained[7] for some complexes in which, as predictable already from energy considerations, an appreciable fraction of the complex stability must be due to exciton interaction.

The strong decrease in intensity of the complex emission has recently been discussed[8] in connection with the results of lifetime measurements on the same complexes in different solvents. It has been found that the mean lifetime of the excited complex, which is of the order of 100 nsec, is shortened by about a factor of three, when the solvent dielectric constant increases from 2 to 12, whereas, at the same time, the relative intensity of the complex emission decreases by about a factor of 40, so that, ultimately, in highly polar solvents like acetonitrile ($\epsilon = 37$) no complex emission at all can be observed (cf. *Figure 5*), although there is strong quenching of the hydrocarbon fluorescence by diethylaniline as indicated by the low half-value quencher concentrations, c_h, given in *Table 1*. The quenching rate constants, k, which can be obtained from these c_h-values, clearly are diffusion-controlled, so that from Eq. (4), using appropriate values for the diffusion coefficients,

$$k = 4\pi N' (D_A + D_D) a \qquad (4)$$

D_A and D_D, one can arrive at values for the encounter distance, a, which range from 4 to 8 Å (column 4 of *Table 1*); N' is the number of molecules per millimole. This distance, if compared with the interplanar separation in excimers and charge-transfer complexes which, generally, is assumed to be $\leqslant 3·5$ Å, seems to indicate that fluorescence quenching can occur in an encounter complex ($^{1*}A \ldots D$) in which the mutual orientation of the molecules is less restricted than in sandwich-type complexes. Consequently, the steric factors involved in the quenching process will not differ too much from unity.

FLASH PHOTOLYSIS†

Flash experiments which have been carried out with strongly quenched solutions ($c_D > 0·15$ M), using a method described elsewhere[9,10], gave transient absorption spectra in which the species: A^-, $^{3*}A$, and D^+ could be identified (see *Table 1*). This suggests the electron-transfer reaction (5)

$$^{1*}A \ldots D \xrightarrow{k_q} A_s^- \ldots D_s^+ \qquad (5)$$
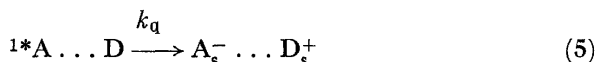
in which a (partially) solvated ion pair is formed, as the prime cause of fluorescence quenching.

† This work was carried out in collaboration with D. Rehm.

*Table 1.* Data on fluorescence quenching and flash photolysis experiments in acetonitrile with D = diethylaniline

A	Half-value concn. of D (M)	k (M^{-1} sec^{-1})	a (Å)	Transient species observed in flash photolysis of quenched solutions	$-\Delta G_q$ (kcal/mole)
Anthracene	0·0096	$2·1 \times 10^{10}$	7·5	A$^-$, ^{3*}A, D$^+$	14
Perylene	0·0081	$2·0 \times 10^{10}$	7·6	A$^-$, ^{3*}A, D$^+$	11
Tetracene	0·0125	$1·2 \times 10^{10}$	4·3	A$^-$, ^{3*}A, —	7
Coronene	0·00017	$1·9 \times 10^{10}$	7·8	A$^-$, — (D$^+$)	5

This ion pair represents a geometrically quite arbitrary encounter complex of the solvated radical ions, both of them being in their characteristic doublet ground states. Its mean lifetime which from the results of the flash experiments could be estimated to be $\leqslant 1\cdot5 \times 10^{-11}$ sec depends on the sum of the rate constants of the reactions by which it can disappear (Eqs 6–8).

(1) Dissociation:

$$A_s^- \ldots D_s^+ \rightarrow A_s^- + D_s^+ \tag{6}$$
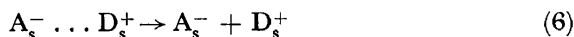
(2) Reversal of electron-transfer leading to triplet state:

$$A_s^- \ldots D_s^+ \rightarrow {}^{3*}A + D \tag{7}$$
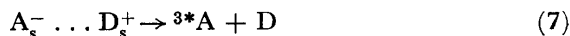
(the triplet state of diethylaniline, being higher up in energy, cannot be reached in this process).

(3) Reversal of electron-transfer leading to ground state:

$$A_s^- \ldots D_s^+ \rightarrow A + D \tag{8}$$

The free energy change, ΔG_q, of reaction (5) can be calculated (according to Eq. 9) from the oxidation potential, $E(D/D^+)$, of diethylaniline, the reduction

$$\Delta G_q = E(D/D^+) - E(A^-/A) - {}^1\Delta E(A) - \frac{e_0^2}{\epsilon a} \tag{9}$$

potential, $E(A^-/A)$, and the singlet excitation energy, $^1\Delta E(A)$, of the hydrocarbon. The last term in Eq. (9) allows for the free energy gained by bringing the ions to encounter distance. Values of ΔG_q, which may be wrong by ± 1 kcal/mole, are given in the last column of *Table 1*. They all are negative, so reaction (5), indeed, will occur spontaneously at least in acetonitrile. This, incidentally, holds true of all aromatic hydrocarbons with the possible exception of pentacene, where ΔG_q, even in acetonitrile, may be slightly positive. In solvents of lower dielectric constant than acetonitrile ΔG_q will, eventually, become positive, so that the rate of reaction (5) will decrease with decreasing dielectric constant of the solvent. However, the rate of complex formation (Eq. 10) which has to compete with reaction (5) will be

$$^{1*}A \ldots D \xrightarrow{k_c} {}^1(A^-D^+) \tag{10}$$
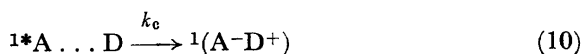
virtually solvent independent, so that the probability of complex formation,

$$\gamma_c = \frac{k_c}{k_c + k_q} \tag{11}$$

γ_c, will strongly decrease with increasing solvent dielectric constant (Eq. 11). It is this solvent dependence of γ_c which essentially determines the relative intensity of the complex emission.

On the other hand, the mean lifetime of the excited complex (being, of course, independent of the probability with which the complex is formed) can depend on solvent polarity through reaction (12) which can be shown

$$^1(A^-D^+) \xrightarrow{k_i} A_s^- \ldots D_s^+ \tag{12}$$
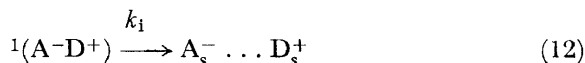
to have $\Delta G_i < 0$ only in polar solvents. However, the effect of this reaction on shortening the life-time of the excited complex is not very pronounced, so one must assume that an appreciable free energy of activation is required in this process, even when ΔG_i is negative.

CHEMILUMINESCENCE†

The idea that the reverse process of reactions (6) and (12) might produce the same type of charge-transfer complexes as does reaction (1) has led us to search for chemiluminescent reactions between anions of aromatic hydrocarbons (A^-) and Wurster's Blue cations (D^+), the oxidized form of tetramethyl-p-phenylenediamine (TMPD), which was used as the perchlorate[11]. The experiments were carried out at room temperature, using dimethoxyethane as the solvent.

Flow experiments, which are described elsewhere[11], enabled us to measure chemiluminescence spectra with the same spectrofluorimeter that was used, also, for the fluorescence spectra, so that the chemiluminescence spectra could be directly compared with the fluorescence spectra of the parent compounds A and D as measured, e.g., after the flow experiment, when electron-transfer according to Eq. (13) was completed. This comparison

$$A^- + D^+ \to A + D \tag{13}$$

clearly showed that the chemiluminescence observed was emitted from the lowest excited singlet states $^{1*}A$ and/or $^{1*}D$.

The enthalpy, $-\Delta H(A^-, D^+)$, released from the electron-transfer reaction (13), can be calculated from the redox-potentials of the A^-/A and D/D^+ couples (measured in acetonitrile) taking into account the entropy change and the difference of the solvation enthalpies in acetonitrile and dimethoxyethane. With all aromatic hydrocarbons used in this chemiluminescence study those enthalpy values turned out to be considerably smaller than the singlet excitation energies, $^1\Delta E(A)$ and $^1\Delta E(D)$, but are about of the same order of magnitude as the triplet excitation energies, $^3\Delta E(A)$ and $^3\Delta E(D)$. So, in order to account for the emission from the excited singlet states which was

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† This work was carried out in collaboration with K. ZACHARIASSE.

observed in most chemiluminescence experiments, triplet–triplet annihilation [Eqs. (16) and (18)] must be invoked.

A more detailed consideration shows that, in fact, three different situations can be envisaged. Situation (14a) which is encountered with non-

$$^3\Delta E(D) > \, ^3\Delta E(A) \qquad\qquad > -\Delta H(A^-,D^+) \qquad (14a)$$

$$^3\Delta E(D) > -\Delta H(A^-,D^+) > \, ^3\Delta E(A) \qquad (14b)$$

$$-\Delta H(A^-,D^+) > \, ^3\Delta E(D) \qquad\qquad > \, ^3\Delta E(A) \qquad (14c)$$

alternant hydrocarbons means that the energy released from the electron-transfer reaction (13) is too low to excite either one of the triplet states. This explains our failure to observe chemiluminescence when fluoranthene negative ion was used for A^-.

On the other hand, the situation (Eq. 14b) which is met with in most of the higher alternant aromatic hydrocarbons implies that the two consecutive steps (Eqs. 15 and 16) can bring about the fluorescence emission of the

$$A^- + D^+ \rightarrow \, ^3{*}A + D \qquad (15)$$

$$^3{*}A + \, ^3{*}A \rightarrow \, ^1{*}A + A \qquad (16)$$

hydrocarbon which, indeed, has been observed in the chemiluminescence experiments[11].

The situation represented by Eq. (14c) applies to biphenyl, naphthalene, triphenylene, and a number of their methyl-substituted derivatives. It means that not only the reactions (15) and (16) can occur, but also reactions (17) and (18) may take place. This explains nicely the simultaneous appearance of

$$A^- + D^+ \rightarrow A + \, ^3{*}D \qquad (17)$$

$$^3{*}D + \, ^3{*}D \rightarrow \, ^1{*}D + D \qquad (18)$$

both the A and D fluorescence emissions in chemiluminescence experiments with naphthalene (cf. *Figure 6*) and with the other hydrocarbons mentioned above. Furthermore, it is only in these cases, where the chemiluminescence spectrum shows A and D fluorescence, that also a structureless long wavelength emission (with maximum around $18\cdot000$ cm^{-1}) has been observed, which unequivocally can be ascribed to the excited charge-transfer complex $^1(A^-D^+)$. We assume that this emission, which also can be found in straightforward fluorescence experiments (but only at very high hydrocarbon concentrations), in the chemiluminescence experiments is brought about by mixed triplet–triplet annihilation (Eq. 19). The possible occurence in

$$^3{*}A + \, ^3{*}D \rightarrow \, ^1(A^-D^+) \qquad (19)$$
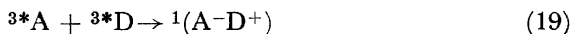
chemiluminescence experiments of triplet emission (phosphorescence), as indicated by the dotted curve in *Figure 6*, has been discussed elsewhere[11].
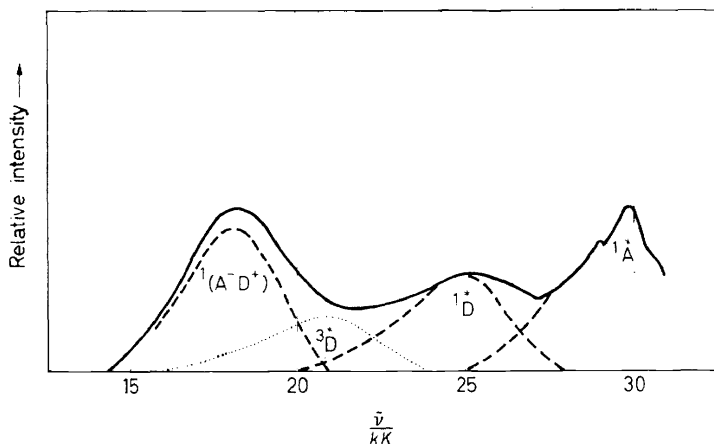
Figure 6. Chemiluminescence spectrum obtained in flow experiments with naphthalene anion $c_A{}^- = 2\cdot6 \times 10^{-3}$ M) and Wurster's Blue perchlorate ($c_D{}^+ = 3 \times 10^{-5}$ M = solubility of WB perchlorate) in dimethoxyethane at room temperature

ACKNOWLEDGEMENT

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