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MO-CALCULATIONS OF THE ENERGY TRANSFER ACTIVITIES OF ORGANIC π-STRUCTURES IN THE PHOTO-FRIES REARRANGEMENT—II

SELECTION OF SENSITIZERS AND INHIBITORS OF THE PHOTO-FRIES REACTION BASED ON THEORETICAL ABSORPTION AND FLUORESCENCE DATA

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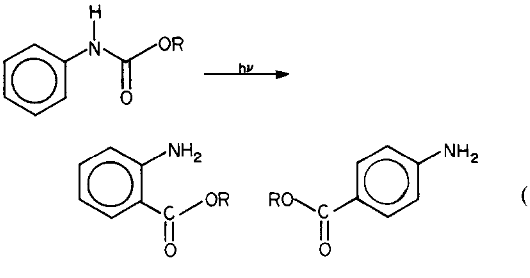
Abstract—Based on quantumchemical PPP-calculations of the absorption and fluorescence maxima for different organic π-systems, carried out in Part I of this series,[1] an assignment of 27 organic molecules as inhibitors or sensitizers in the photo-Fries reaction has been made. The consideration involves also π-systems, which should be able to influence the reaction due to their higher excited singlet states. The results obtained are in fair agreement with the experimental facts and allow, moreover, to suggest some kinds of structures which should act as energy donors or acceptors in the photo-Fries reaction, without having been checked emperimentally so far.

The SCF–SC(β^*)–LCI–method, suggested by Fratev *et al.*[2,3] has been used successfully to estimate the fluorescence maxima of a large number of organic π-systems with very different topologies in the previous paper of the series.[1] Together with the good reproduction of the absorption maxima of organic π-systems by an adequate PPP-procedure these results enable us to assign the π-conjugated molecules (M) treated theoretically as potential sensitizers, inhibitors or inefficient species in the photo-Fries reaction (1) of N-phenylurethane (NPU).



(1)

Provided the molecule M is photochemically stable enough, the main condition that it is active to be a donor or an acceptor of excitation energy in the photo-Fries reaction (1) is simply:

$\tilde{\nu}^{abs}_{NPU} \leq \tilde{\nu}^{fl}_{M}$ sensitizer M (i)

$\tilde{\nu}^{fl}_{NPU} \geq \tilde{\nu}^{abs}_{M}$ inhibitor M (ii)

$\tilde{\nu}^{fl}_{M} < \tilde{\nu}^{abs}_{NPU}$ or $\tilde{\nu}^{fl}_{NPU} < \tilde{\nu}^{abs}_{M}$ inefficient M. (iii)

In the following section an attempt will be made to systematize some π-systems in view of their potential behaviour in the photo-Fries reaction.

RESULTS AND DISCUSSION

The region of the NPU absorption begins at 34.8 kK.[4] PPP-calculations provide a vertical transition energy of 35.9 kK in close agreement with the maximum of the longest wavelength absorption band. Consequently, compounds with fluorescence maxima between 39 and 35 kK should be able to deliver their excitation energy to the lowest excited singlet level of NPU. Even compounds with fluorescence maxima between 41 and 44 kK can act as donors of energy in reaction (1), for a transfer into the S_2-level of NPU (calculated at 40.8 kK) should be possible.

In Fig. 1 some molecules are collected which should be able to sensitize the photo-Fries reaction. For benzene and toluene this result is closely confirmed by extended experimental investigations.[5,6] For other structures no results are available. It should be mentioned, moreover, that for the heterocyclic sensitizers in the lower part of Fig. 1 very short fluorescence lifetimes should be predicted, due to their high emission energies. This follows from the relation of the fluorescence lifetime τ and the wave number $\tilde{\nu}$ of the absorption as well as the oscillator strength:[7]

$$\tau = \frac{1.5}{f \cdot \tilde{\nu}^2}. \qquad (2)$$

This fact should increase their efficiency. Until now no fluorescence spectra are known for the simple heterocyclic compounds like thiophene, furane and thiazole.[8]

Much more interesting from the practical point of view (*cf.* Part I[1]) are those π-systems with absorptions within the region of fluorescence of NPU. These compounds are arranged in Fig. 2. The maximum of the NPU fluorescence has been predicted at 33.8 kK in excellent agreement to the experimental fluorescence spectrum measured recently.[6] Potential inhibitors of (1) therefore, are molecules with absorption maxima between 30 and 35 kK. Fundamentally, also molecules with higher singlet energy levels in this region should be able to quench the photo-Fries reaction. Here the transfer of energy into any S_i state will be followed by a fast radiationless relaxation to S_1. Some examples of this case are shown in Fig. 3. Due to a normally very large intensity of the high energetic absorption bands, also very large values for the integral

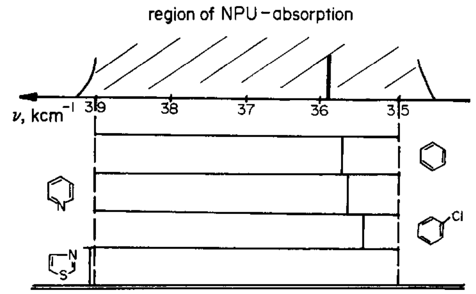


Fig. 1. Calculated fluorescence maxima of some selected π-systems, positioned within the region of the NPU absorption. These molecules should sensitize the photo-Fries reaction.

U can be expected[8] (*cf.* Part III). Also this fact seems to favour the quenching activity of these molecules. On the other hand, it should be emphasized that only colourless substances are acceptable as inhibitors of (1) from the practical point of view. Therefore, the longest wavelength absorption band of such compounds should not exceed 350 nm.[9]

The list in Fig. 2 contains also salicylic aldehyde, salicylic acid and dibenzofurane, which have been found to be quenching systems of high efficiency[6] in the photo-Fries reaction. It is further interesting that also anthranilic ester, one of the main photoproducts of reaction (1) should act as a quencher, especially in protic solvents. This gives a hint to a possible self-quenching of the photo-Fries reaction, which is in agreement with the experimental fact of an incomplete course of the photorearrangement.[10] On the other hand also the filter effect of the ortho-product should be responsible for this finding.[10]

In protic solvents a bathochromic shift of the NPU-fluorescence has been observed.[6] Thus, those potential quenchers with their absorption maxima at the low energy end of the NPU-fluorescence in Fig. 2 (arranged in the lower part of the Fig. 2) should have a strong effect in this medium and even in the solid state, whereas the compounds in the upper part of Fig. 2 should lose or at least diminish their activity. In this respect especially the 2-(*ortho*-hydroxy)-phenyl 5-membered ring heterocycles should be noticed. These compounds has been found to be highly photostable[11] due to their dissipation of transition energy by an intramolecular proton transfer.[12–17] Indeed, some of them together with similar systems have been

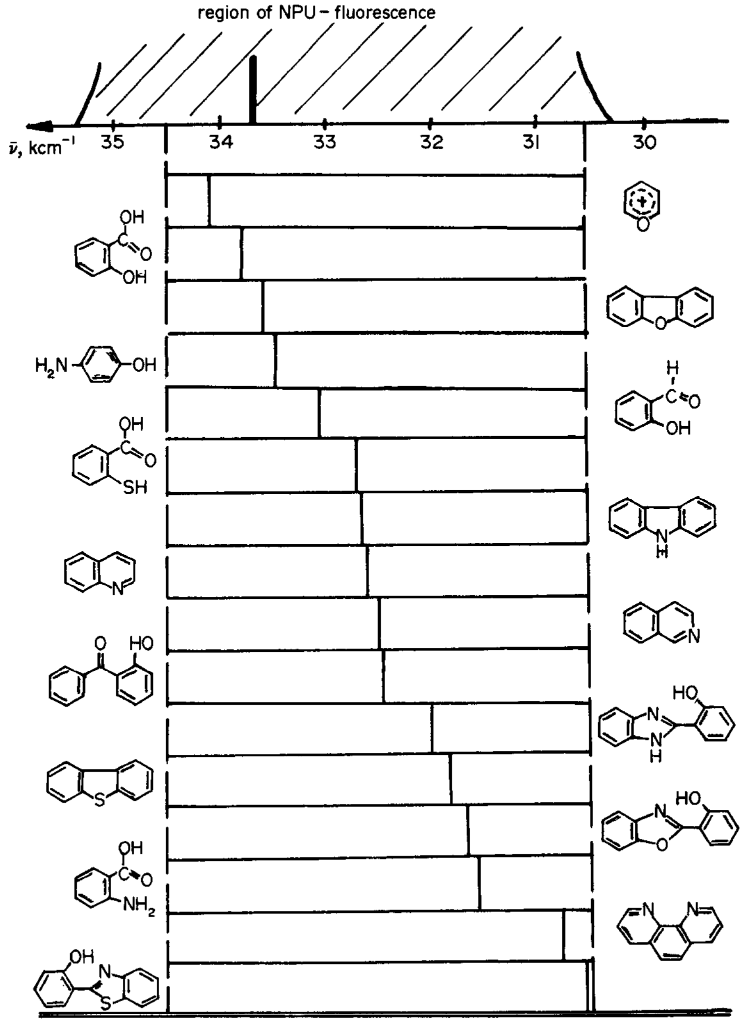


Fig. 2. Calculated absorption maxima of some selected π-systems, positioned within the region of NPU fluorescence. These molecules should inhibit reaction (1).

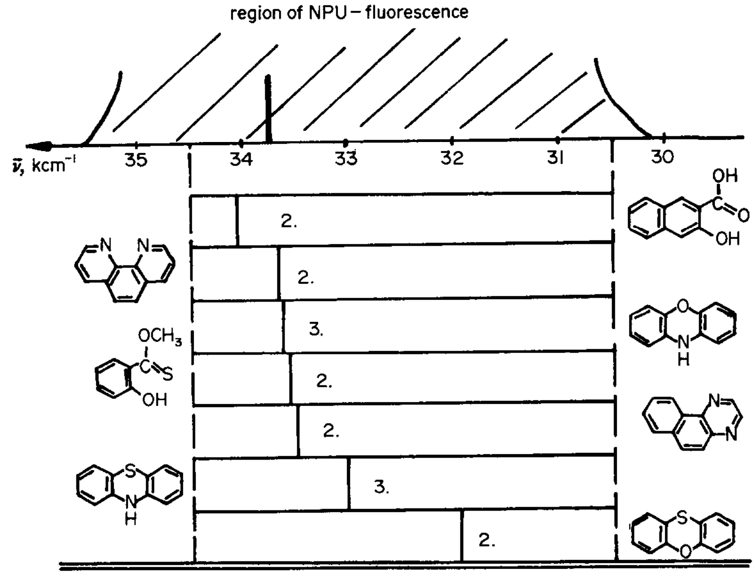


Fig. 3. Several examples of the approximate coincidence between higher levels of absorption in some π-systems and the fluorescence transition of NPU. These molecules should also inhibit reaction (1).

tested to act as "UV stabilizers" in model compounds[18–20] and polymers.[21–30] Their acting mechanism is described to be not quite clear[24] and it seems, that the ability of forming H-bonds should take an important role for the inhibiting mechanism[29,30] This is due to a stabilization effect of the CN-bond in the substrate molecule in its first excited state.[31] Nevertheless, the ability of these compounds to act additionally as acceptors of energy from NPU is clearly supported by these investigations.

Among the compounds collected in Figs. 1–3 a variety of organic π-systems has been investigated. The result was an assignment to the group (iii), for these compounds had not suited absorption properties to act as a quencher in the photo reaction (1). The quantum chemical model used, however, enables us to estimate those topological variations, necessary to shift the longest wavelength absorption band into the fluorescence region of the NPU-molecule. In this way an "ideal quencher" of (1) can be constructed.

On the other hand, a more profounded assignement of any molecule to be an effcient sensitizer or inhibitor of the reaction (1) involves the calculation of the pseudo-Coulomb integral U[7] as the second important variable in the energy transfer process. This will be done in Part III of the series.

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