Tetrahedron Vol. 34, pp. 481 to 486. Pergamon Press 1978. Printed in Great Britain

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

A THEORETICAL INDEX FOR THE ENERGY TRANSFER EFFICIENCY OF ORGANIC π-SYSTEMS IN THE PHOTO-FRIES REACTION

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(*Received in UK* 19 *July* 1977; *Accepted for publication* 8 *August* 1977)

Abstract—The energy transfer process between the excited singlet state of N-phenylurethane, NPU*, and any other π-system, M, will be described theoretically by introducing the integral U, which symbolizes the interaction of the states NPU*-M and NPU-M* following a suggestion of Labhart *et al.*[1] The formula for U based on the LCAO-MO-SCF-LCI approximation in the Pariser-Parr-Pople-version enables us to systematise the energy tranfer tendency of any π-system to quench or sensitize the photo-Fries reaction of NPU* depending on the aggregate geometry NPU-M. The criteria of the complex geometry and the electronic structure of M providing a maximal value of U are collected and discussed. Together with the differences in transition energies of the fluorescence and the absorption spectra of NPU and M, respectively, the maximal values of U yield a theoretical index ρ, providing a sequence for different M to inhibit the photo-Fries reaction by energy acception.

Based on the approximate coincidence of absorption and fluorescence spectra, in Part II of the series,[2] a number of organic π-systems has been found, which can act as inhibitors or sensitizers of the photo-Fries reaction[3] within an energy transfer process. The transition energies of absorption and fluorescence were obtained by using the Pariser-Parr-Pople (PPP)-procedure. This method is well established for calculating the electronic transitions in absorption spectra[4] and has been modified recently[5-7] to estimate the emission energies.

On the other hand, the probability of the energy transfer depends strongly on an integral U, which represents a "pseudo-Coulombic" interaction between the transition densities of, e.g. N-phenylurethane, NPU, the molecule of our basic interest, and any π-system, M, which should influence the photoreaction of the former. In a compact version U is given by eqn (1)

$$U = \langle \Phi_{NPU^*}\Phi_M|\hat{V}|\Phi_{NPU}\Phi_{M^*}\rangle \qquad (1)$$

where the Hamiltonian $\hat{V}$ contains all interactions between the initial and final state of the supermolecule NPU-M, the wave function of which has been expressed as the product of the unperturbed many electron functions of the component systems. U holds within our simple model for the second important variable of the probability of the energy transfer, but has not been taken into account for a qualification of the π-systems in Part II. In this paper, therefore, an approximate expression for U will be derived based on a suggestion made by Labhart *et al.*[1] This expression contains only variables, available from ordinary PPP-calculations and enables us to calculate U for any geometry of the aggregate NPU-M in relation to the electronic structure of both components in the ground and excited singlet state.

The relation between U^2 and the difference of the absorption and fluorescence energies, ΔΔE, for obtaining a theoretical measure for the energy transfer should be given in analogy to an equation derived by Foerster[8] as

$$\rho = \frac{8U^2}{h}[\Delta E^a - \Delta E^{abs} + 4U^2]^{-(1/2)}. \qquad (2)$$

Here, ρ, will be defined as a theoretical index of the energy transfer probability, the value of which represents a key for systematising organic π-systems that can influence the photo-Fries reaction as a donor or an acceptor of energy.

Expansion of the interaction integral U

Starting from eqn (1) the many electronic functions can be expressed by a linear combination of the configurational wave functions

$$\Psi_{NPU^*\text{-}M} = \sum_{\substack{i\to j\\ \in NPU}} C_{i\to j}\Psi^{NPU}_{i\to j}\Psi_o{}^{M} = \sum_{i\to j} C_{i\to j}\Psi^{NPU^*\text{-}M}_{i\to j} \qquad (3)$$

and

$$\Psi_{NPU\text{-}M^*} = \sum_{\substack{k\to l\\ \in M}} C_{k\to l}\Psi^{M}_{k\to l}\Psi_o{}^{NPU} = \sum_{k\to l} C_{k\to l}\Psi^{NPU\text{-}M^*}_{k\to l} \qquad (4)$$

with

$$\Psi^{NPU^*\text{-}M}_{i\to j} = \left(\frac{1}{2}\right)^{1/2}\{|\psi_{1,NPU}\bar{\psi}_{1,NPU}\cdots\psi_{i,NPU}\bar{\psi}_{j,NPU}\cdots\psi_{n,NPU}\bar{\psi}_{n,NPU}\psi_{1,M}\bar{\psi}_{1,M}\cdots\psi_{m,M}\bar{\psi}_{m,M}| - |\psi_{1,NPU}\bar{\psi}_{1,NPU}\cdots\bar{\psi}_{i,NPU}\psi_{j,NPU}\cdots\psi_{n,NPU}\bar{\psi}_{n,NPU}\psi_{1,M}\bar{\psi}_{1,M}\cdots\psi_{m,M}\bar{\psi}_{m,M}|\}. \qquad (5)$$

In eqns (3) and (4), $C_{i\to j}$ and $C_{k\to l}$ label the component eigenvectors of a one electron transition $\psi_i\to\psi_j$ in NPU and $\psi_k\to\psi_l$ in M, resulting from the matrix of configuration interaction, respectively. The bars above the mole-

cular orbitals in eqn (5) indicate occupation by an electron with β spin.

The operator $\hat{V}$ in eqn (1) contains all the interactions between the states NPU*–M and NPU–M* and becomes:

$$\hat{V} = \sum_{\substack{A,B \\ \in NPU \in M}} H^c_{AB} + \sum_{A>B} \frac{e^2}{R_{AB}}. \quad (6)$$

Insertion of eqns (3)–(6) into (1) and expansion of the integral provides (7):[7]

$$U = \sum_{\substack{i,j \\ \in NPU}} \sum_{\substack{k,l \\ \in M}} C_{i\to j} C_{k\to l} \{[S_{ik}H_{jl} + S_{jl}H_{ik} + S_{jk}H_{il} + S_{il}H_{jk}] + (ij/kl) - (ik/jl)\}. \quad (7)$$

The terms in eqn (7) can be defined and expanded by a linear combination of the atomic orbitals within the two π-systems as following:

$$S_{rs} = \langle \psi_r | \psi_s \rangle = \sum_{\mu \in NPU, \nu \in M} c_{\mu r} c_{\nu s} S_{\mu\nu}. \quad (8)$$

$$H_{rs} = \langle \psi_r | H^c | \psi_s \rangle = \sum_{\mu \in NPU, \nu \in M} c_{\mu r} c_{\nu s} H_{\mu\nu} \quad (9)$$

with

$$\langle \phi_\mu | H^c | \phi_\nu \rangle = K \cdot S_{\mu\nu} = H_{\mu\nu} \quad (10)$$

$$(rs/tu) = \left\langle \psi_r(1)\psi_s(1) \frac{e^2}{R_{12}} \psi_t(2)\psi_u(2) \right\rangle$$

$$= \sum_{\substack{\mu,\rho \\ \in NPU}} \sum_{\substack{\nu,\sigma \\ \in M}} c_{\mu r} c_{\rho s} c_{\nu t} c_{\sigma u} (\mu\rho/\nu\sigma). \quad (11)$$

Introduction of the zero differential overlap approximation into eqn (11) and insertion of eqns (8)–(11) into eqn (7) gives the final expression for the integral U:

$$U = \sum_{\substack{i,j \\ \in NPU}} \sum_{\substack{k,l \\ \in M}} C_{i\to j} C_{k\to l} \sum_{\substack{\mu \\ \in NPU}} \sum_{\substack{\nu \\ \in M}} c_{\mu i} c_{\mu j} c_{\nu k} c_{\nu l} \times \left[\gamma_{\mu\nu} + 4KS^2_{\mu\nu} - \frac{1}{4} S^2_{\mu\nu} \left(\sum_\mu \sum_\nu c^2_{\mu i} c^2_{\nu l} \gamma_{\mu\nu} \right) \right]. \quad (12)$$

In eqn (12) $\gamma_{\mu\nu}$ is the two centre electronic repulsion integral

$$\gamma_{\mu\nu} = \left\langle \phi_\mu(1)\phi_\mu(1) \frac{e^2}{R_{12}} \phi_\nu(2)\phi_\nu(2) \right\rangle \quad (13)$$

which has been estimated by using the Mataga–Nishimoto approximation.[9]

In a short hand notation eqn (12) can be expressed as:

$$U = U_C + U_R + U_E \quad (14)$$

with:

$$U_C = \sum_{\substack{i,j \\ \in NPU}} \sum_{\substack{k,l \\ \in M}} C_{i\to j} C_{k\to l} \sum_{\substack{\mu \\ \in NPU}} \sum_{\substack{\nu \\ \in M}} c_{\mu i} c_{\mu j} c_{\nu k} c_{\nu l} \gamma_{\mu\nu} \quad (15)$$

$$U_R = 4K \sum_{\substack{i,j \\ \in NPU}} \sum_{\substack{k,l \\ \in M}} C_{i\to j} C_{k\to l} \sum_{\substack{\mu \\ \in NPU}} \sum_{\substack{\nu \\ \in M}} c_{\mu i} c_{\mu j} c_{\nu k} c_{\nu l} S^2_{\mu\nu} \quad (16)$$

$$U_E = \frac{1}{4} \sum_{\substack{i,j \\ \in NPU}} \sum_{\substack{k,l \\ \in M}} C_{i\to j} C_{k\to l} \sum_{\substack{\mu \\ \in NPU}} \sum_{\substack{\nu \\ \in M}} c_{\mu i} c_{\mu j} c_{\nu k} c_{\nu l} S^2_{\mu\nu} \times \sum_\mu \sum_\nu c^2_{\mu i} c^2_{\nu l} \gamma_{\mu\nu} \quad (17)$$

Here U_C, U_R and U_E represent the change of coulombic repulsion between the electrons of the two states, of the resonance interaction between the electrons in NPU and the core in M and vice versa and of the energy of exchange of electrons between the two states according to a localization of the excitation on NPU or on M, respectively.

It can be shown, that the first term in eqn (14) is the dominant one. The second term, due to the resonance interactions is smaller for one order of magnitude. The third term U_E is still much smaller and can be neglected for the first approximation. Thus, for a rough estimation of the U integrals for different systems in different geometries the exclusive consideration of the term U_C should be sufficient and has been applied elsewhere.[10–12] From eqn (12) it can be seen that U becomes zero, if the transition in M creating M* is forbidden.

Variation of U with the spatial arrangement of the complexing molecules

The variables $\gamma_{\mu\nu}$ and $S_{\mu\nu}$ in eqn (12) cause a considerable dependence of the integral U on the spatial arrangement of the component molecules in the aggregate. In physical mixtures of the components in solution or in the gas phase, U will be obtained as a statistical average value of all configurations existing incidentally in the moment of the energy transfer process. This has been taken into account, e.g. in the Foerster equation by introducing the orientation factor κ, which reduces the product of the transition moment vectors.[8] In the case of a nonconjugative coupling of the partners[13–15] and even in the solid state, however, the efficiency of the energy transfer should be determined by the fixed spatial arrangement of the components. It seemed to be desirable for us, therefore, to know the dependence of U on definite geometries of the aggregates. Thus, for the complex NPU-pyrrole a systematical variation of the geometrical arrangement in view of the following degrees of freedom has been made:

(i) *The complex has a planar geometry.* The pyrrole molecule surrounds the NPU-ring within its plane (see Fig. 1a).

(ii) *The complex has a sandwich geometry.* The distance of the planes was varied (Fig. 1b). The translating movement of the pyrrole molecule relative to the NPU within a fixed distance of the planes has been investigated (Fig. 1c). The rotating movement of the pyrrole molecule relative to NPU within a fixed distance of the planes and a fixed arrangement of the pyrrole over the π-system of NPU was checked (Fig. 1d).

The results of the study are the following:

(i) U^2 for sandwich complexes exceeds that of planar complexes for 2–3 orders of magnitude.

(ii) U^2 shows an exponential slope with R and becomes infinite in the case of the united molecules. Therefore, the optimal intermolecular distance of the two molecules in the sandwich arrangement should collapse with the optimal value of U^2.

(iii) Maximal overlapping of the two π-systems causes

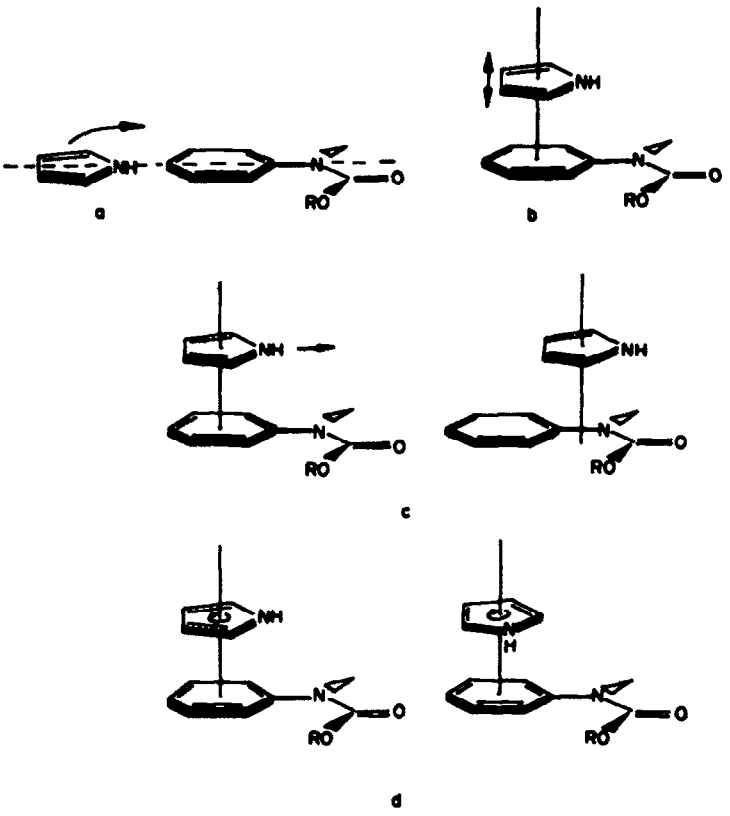


Fig. 1. Models of different spatial arrangements of NPU and pyrrole in the study of the spatial influence on the value of U: (a) planar complex; (b) sandwich complex with different distances of the planes; (c) sandwich complex, pyrrole moves over NPU; (d) sandwich complex, pyrrole rotates around the given axis.

a maximal value of U^2. Thus, the complex "ring over ring" is more favourable than the complex "ring over functional group".

(iv) Within a fixed distance of the molecular planes and the optimal overlapping of the π-systems U^2 will be further dependent on the angle ϑ formed by the transition moments of the two π-systems, which are available from PPP calculations, too. U^2 becomes a maximum for $0 \leqslant \vartheta \leqslant 15$ and $160 \leqslant \vartheta \leqslant 180°$ (see Fig. 2).

The relation between U^2 and ρ given in eqn (2) indicates, that based on the total or approximate coincidence of the absorption and fluorescence transition energies of NPU and M, a maximal value of U^2 means a maximal ability of M to stimulate or inhibit the photo-Fries reaction. To obtain a reliable sequence of U values for different systems M, only those geometries of the aggregate NPU–M will be considered which gave maximal values for U^2. The geometry considered is therefore at the same time the most favourable position of M relative to NPU in the energy transfer process.

Calculation and discussion of the new index ρ

According to eqn (15) the maximum values of U have been calculated for an extended number of π-systems being under discussion for sensitising or inhibiting the photo-Fries reaction. It has been found that U is subject to considerable variations due to the topology of M. Figure 3 shows the region comprising U^2 for different molecules considered. Whereas the pyrylium ion and the small 5-membered heterocyclic rings provide rather high values of U^2, the more extended π-systems have often U^2-values of two orders of magnitude lower than the former. To this group of molecules belongs also dibenzofurane, which is known to be an effective inhibitor of the photo-Fries reaction[16] (see below). This example shows, as we know from eqn (2), that U^2 cannot be the only variable for estimating the energy transfer activities.

Thus, calculating the theoretical index ρ according to eqn (2) we combine the theoretical results for the differences in absorption and fluorescence energies of the two molecules (see Part II) and the U-values obtained from eqn (15). Then, ρ represents within the scope of our approximate model, the ability of any π-system to act as donor or acceptor of the excitation energy of NPU.

Table 1 shows the results. In excellent agreement with the experiment we find that the salicylic ester and dibenzofuran are the chief inhibitors of the photo-Fries reaction.[16] Also the photoproduct of the reaction, anthranilic ester should have considerable ability to act as quencher of the reaction. However, the most superior quenching system for the reaction has been found to be the pyrylium ion. This system has not been tested at all.

The striking differences in the sequence of systems between Table 1 and Fig. 3 show, as mentioned above, that small values of U^2 cannot be combined in every case with a low transfer ability of the system and *vice versa*. The deciding fact of a high quenching or stimulating effect is both a high value for U^2 and a low difference between the emission energy of donor and the absorption energy of the acceptor. A good example is dibenzofuran, the excellent quenching activity of which is mainly due to a small energy difference of its long wavelength

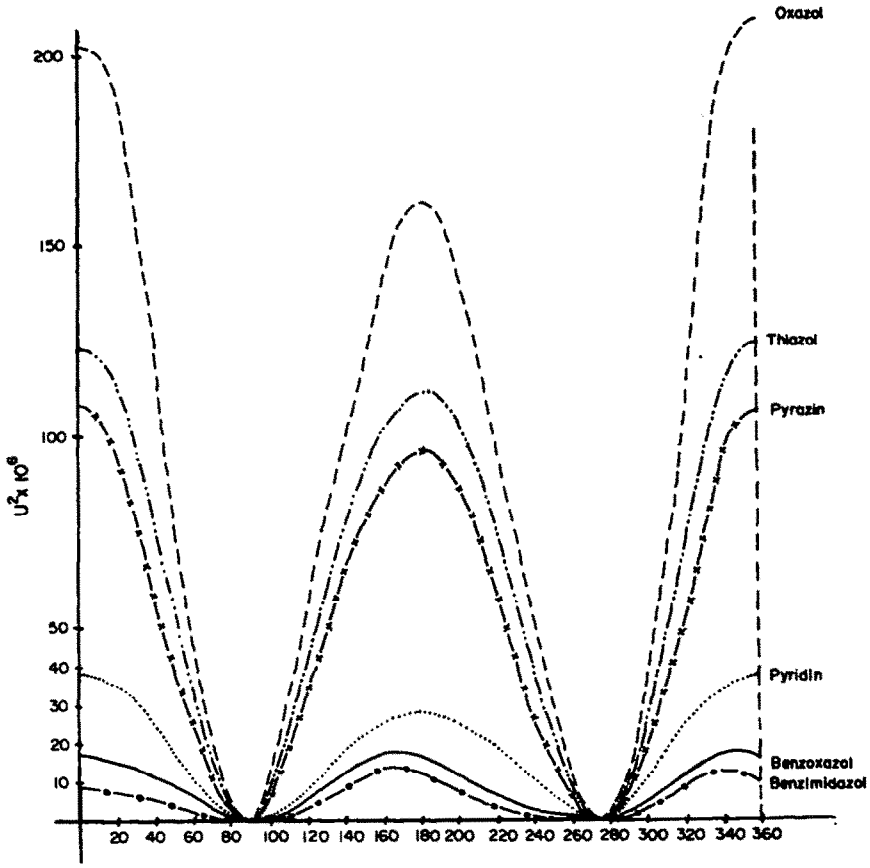


Fig. 2. The influence of the rotation angle on U^2 for different systems.

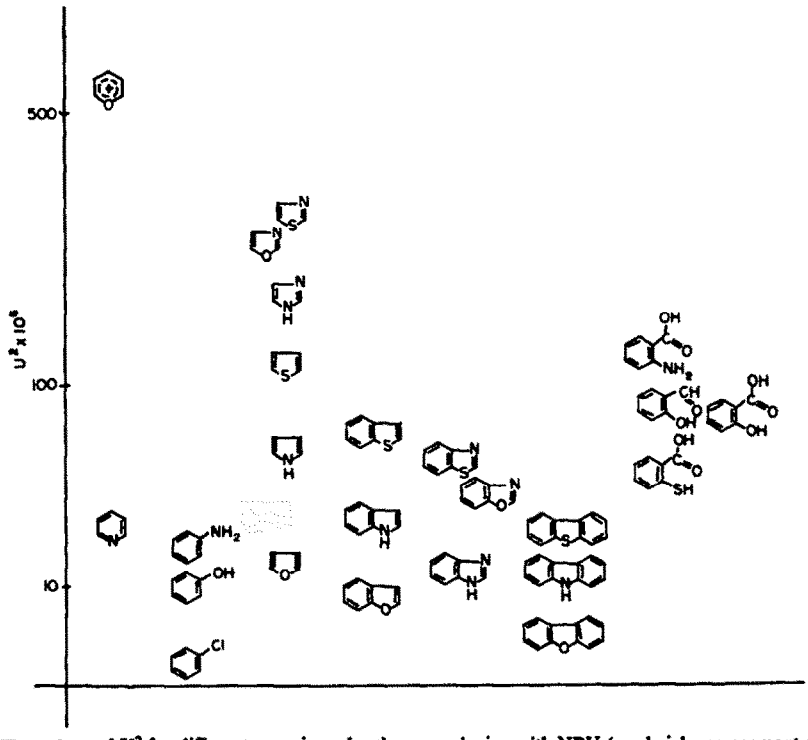
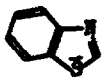
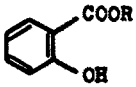
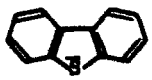
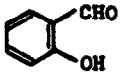
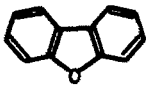
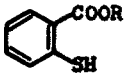
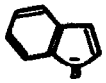
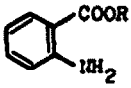
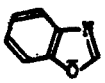
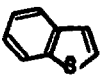
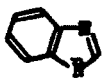
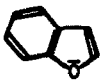
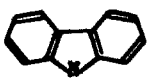


Fig. 3. The values of U^2 for different organic molecules, complexing with NPU (sandwich arrangement optimized, distance of the planes: 3.5 Å).

Table 1. Calculated ρ-values for selected π-systems and their action mode to the photo-Fries reaction.
(1) quenchers
(2) sensitizers
} of the photo-Fries reaction.

Compound	ρ · h · 10⁴ [eV]	action mode	Compound	ρ · h · 10⁴ [eV]	action mode
	630	Q[1]		9	Q
	230	Q		9	Q
	79	Q		8	S
	47	Q		8	S
	37	Q		5	Q
	33	Q		4	Q
	23	Q		4	Q
	20	S[2]		2	Q
	10	S		2	S
	10	Q		1	S

absorption band to the location of the NPU fluorescence. On the other hand, the 5-membered ring heterocycles should have only a small sensitizing activity, although their U^2-values are rather high. In the case of pyrylium both a large value of U and a small energy difference is predicted.

The model suggested seems to reflect some relevant relations concerning the energy transfer phenomenon in the photo-Fries reaction, in spite of some drastic approximations. Therefore, it can be helpful for a systematic search of inhibitors of the reaction investigated. The expenses for obtaining the results are rather small and at least a rough selection of structures for practical tests can be given. In Fig. 4 the transition energies and the transition moments (which can be shown to be in a nearly direct proportionality to U^2) of some π-systems are presented in comparison to the emission energy of NPU. Nearly all the systems are unchecked, but should have a quenching effect on the photo-Fries reaction. Attention had been given to a minimal difference in the excitation energy to the emission energy of NPU, to high transition moments and to a sufficient photostability of the systems. The number of compounds considered can be extended arbitrarily and the model presented can be transformed to other photoreactions, the stimulation or anihilation of which is of practical interest.

REFERENCES

[1] H. Labhart, E. R. Pantke and K. Seybold, *Helv. Chim. Acta* **55**, 658 (1972).
[2] A. Mehlhorn, B. Schwenzer and K. Schwetlick, *Tetrahedron* **33**, 1489 (1977).
[3] D. Bellus, *Adv. Photochem.* **8**, 109 (1971).
[4] K. Ohno, *Adv. Quant. Chem.* **3**, 240 (1967).
[5] F. Pratev, G. Hiebaum and A. Gochev, *J. Mol. Struct.* **23**, 137 (1974).
[6] F. Pratev and A. Tadler, *Ibid.* **27**, 185 (1975).

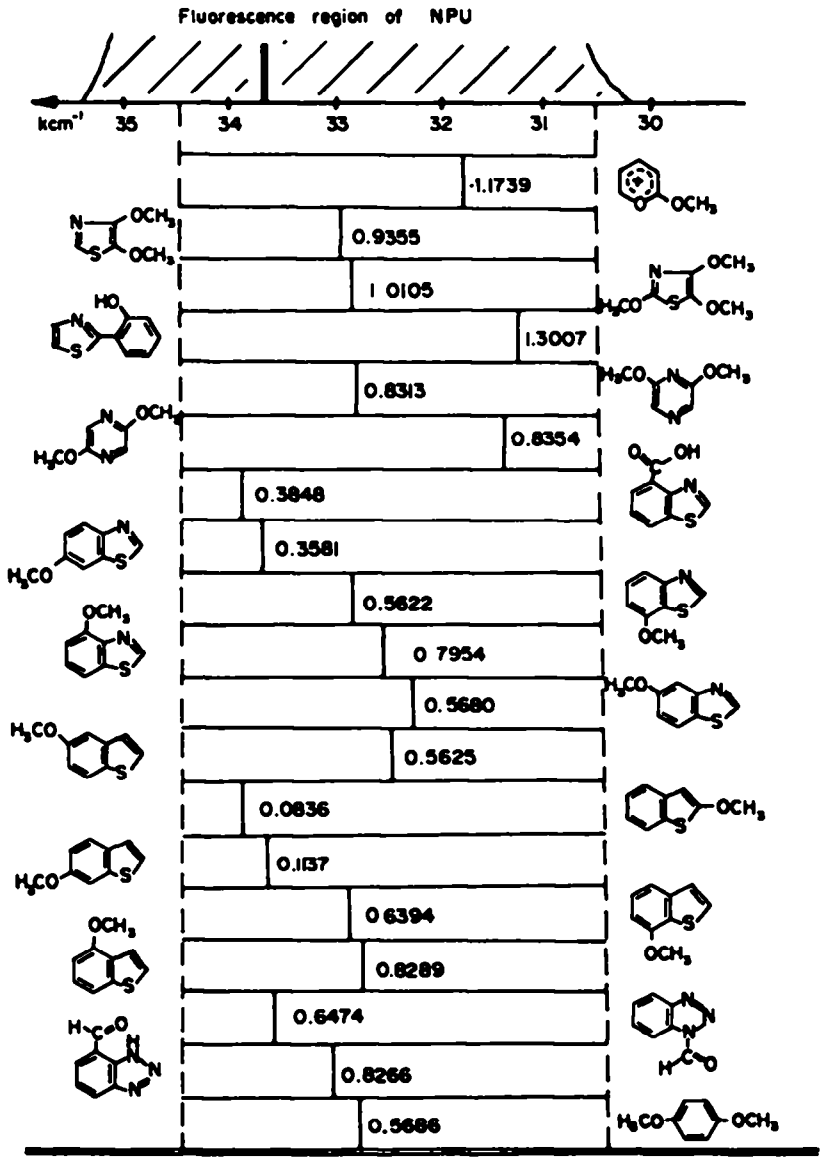


Fig. 4. Potential quenchers of the photo-Fries reaction, not tested so far.

[7]A. Mehlhorn, B. Schwenzer and K. Schwetlick, *Tetrahedron* 33, 1483 (1977).
[8]Th. Förster, *Modern Quantum Chem.* 3, 93 (1965).
[9]N. Mataga and K. Nishimoto, *Z. Phys. Chem.* 13, 140 (1957).
[10]F. Dietz, K.-J. Plässer and N. Tyutyulkov, *Z. Chem.* 12, 144 (1972).
[11]J. L. Magee, *Comparative Effects of Radiation*, p. 130. Wiley, New York (1960).
[12]I. G. Kaplan and V. G. Plotnikov, *Chimiya Vysokich Energii* 1, 507 (1967).
[13]O. Schnepp and M. Levy, *J. Am. Chem. Soc.* 84, 172 (1962).
[14]A. A. Lamola, *Technique of Organic Chemistry* (Edited by A. Weissberger), Vol. XIV, pp. 17. Interscience, New York (1969).
[15]R. A. Keller and L. J. Dolby, *J. Am. Chem. Soc.* 89, 2768 (1967).
[16]J. Stumpe, R. Noack and K. Schwetlick, to be published.