Tetrahedron. Vol. 33, pp. 1483 to 1488. Pergamon Press 1977. Printed in Great Britain

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

ESTIMATION OF THE ENERGY LOWERING IN THE FIRST EXCITED SINGLET STATE DUE TO A GEOMETRICAL RELAXATION OF THE π-SKELETON

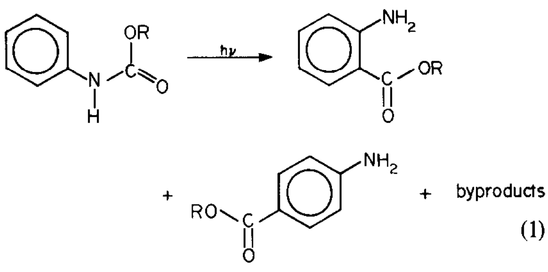
A. MEHLHORN, B. SCHWENZER and K. SCHWETLICK*
Sektion Chemie der Technischen Universität, DDR-8027 Dresden, Mommsenstr. 13, DDR

(*Received in the UK* 16 *November* 1976; *Accepted for publication* 13 *December* 1976)

Abstract—Based on the consideration that the energy transfer between two molecules is in close connection to the position of their absorption and fluorescence bands, the energy lowering of the first excited singlet state due to a geometrical relaxation has been estimated for 40 π-systems. A modified SCF-variable β^*-technique given elsewhere[1] has been used. The selection of the compounds treated has been carried out in view of their potential activity in the photo-Fries reaction to be donors or acceptors of energy. The results obtained are in good agreement with the absorption and fluorescence spectra even for compounds, which undergo a tautomerism in their excited states.

1. INTRODUCTION

The photo-Fries reaction, highly important as an initial step in the photodecomposition of polymers containing N-arylamido groups, has been investigated very intensely during the last years at the model monomer N-phenylurethane NPU:[2-9]



(1)

The quantum yield of the reaction (1) can be influenced by other molecules in a sensitizing or inhibiting way.[10]

$$\mathrm{NPU} \rightarrow \mathrm{NPU}^* \qquad (2)$$

$$\mathrm{NPU}^* + \mathrm{M} \rightarrow \mathrm{NPU} + \mathrm{M}^* \qquad (2a)$$

$$\mathrm{M}^* \rightarrow \mathrm{M} + h\nu \quad \text{(or radiationless deactivation)} \qquad (2b)$$

Therefore, polymers of the corresponding structure may be stabilized by additives to prevent the reaction (1) or their resultant steps. The most elegant effect of such inhibitors would be the acceptance of the excitation energy from the absorbing species by an energy transfer process and the annihilation of this energy by radiationless deactivation or luminescence. The detection of such "ideal inhibitors" of (1) was until now the result of rather time-consuming empirical test series.

In the following papers an attempt will be made to find molecular structures, suited optimally as energy acceptors or donors in the reaction (1) and therefore able to quench or to sensitize the photo-Fries rearrangement, purely theoretically. This will be done by applying semiempirical methods of quantum chemistry simple enough to be tractable also for large molecules of practical interest.

2. MODEL, PROCEDURE, COMPOUNDS TREATED

Provided that the distance between NPU and M is large enough, one can assume that the supermolecule NPU-M can be described in its decisive situations NPU*-M and NPU-M* by the products of the total electronic wave functions $\Phi_{NPU^*}\Phi_M$ and $\Phi_{NPU}\Phi_{M^*}$ respectively.

Starting from the initial state $\Phi_{NPU^*}\Phi_M$ the transfer rate $n_{NPU\rightarrow M}$ will be given as the quotient of the expectation value of the final state $\Phi_{NPU}\Phi_{M^*}$ derived from the time-dependent Schrödinger equation and the time. Using the simple exciton model, $n_{NPU\rightarrow M}$ for the strong coupling case becomes:[11]

$$n_{NPU\rightarrow M} = \frac{8U^2}{h}[(W_{NPU^*\text{-}M} - W_{NPU\text{-}M^*})^2 + 4U^2]^{-1/2} \qquad (3)$$

where

$$W_{NPU^*\text{-}M} - W_{NPU\text{-}M^*} = \Delta\Delta E \qquad (4)$$

corresponds to the difference in the excitation energies of NPU and M. U is defined as a pseudo-Coulomb interaction integral of the transition densities in the initial and the final state:

$$U = \langle \Phi_{NPU^*}\Phi_M|\hat{V}|\Phi_{NPU}\Phi_{M^*}\rangle \qquad (5)$$

where $\hat{V}$ includes all interactions between the parts of the supermolecule in the two different states.

Refinement of the model by including the vibrational movement of the nuclei and integration over continuous Boltzmann functions provides to a modified result for large molecules in dense media:[11] For both the strong as the very weak coupling cases, the energetic neighbourhood of the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor together with the integral U are the most important variables in estimating $n_{NPU \to M}$.

A powerful model for a theoretical approach of the energy transfer ability between NPU and another π-system M has therefore the following requirements:

(i) A reliable possibility to calculate at least the maxima of absorption or fluorescence spectra of any organic π-system (this paper);

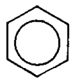
(ii) A selection of sensitizers and inhibitors of the photo-Fries reaction based on their absorption and emission maxima in comparison to those of NPU (Part II);

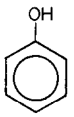
(iii) Calculation of U as a function of the electronic structure of NPU and M and in dependence on their spatial arrangement;

(iv) Based on the results of (ii) and (iii), selection of the most favorable topologies able to quench optimally the photo-Fries reaction by energy transfer (Part III).

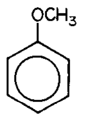
Realizing step (i), a short report on the calculation of the fluorescence and absorption maxima of the compounds listed below should be given.

The molecules considered are divided into three classes: mono-substituted benzenes (**1**), heterocyclic 5- and 6-membered rings (**2**) and molecules of both classes showing an anomalous Stokes-shift due to prototropic processes in their excited states (**3**).

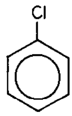

1-1



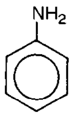
1-2



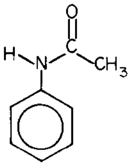
1-3



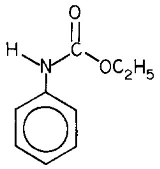
1-4



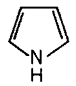
1-5



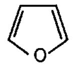
1-6



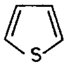
1-7



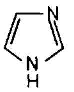
2-1



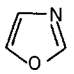
2-2



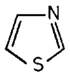
2-3



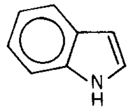
2-4



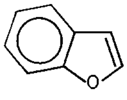
2-5



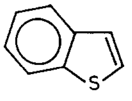
2-6



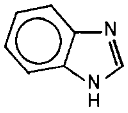
2-7



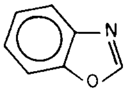
2-8



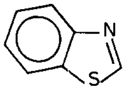
2-9



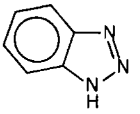
2-10



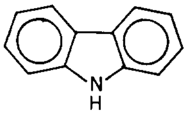
2-11



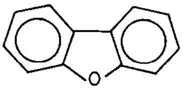
2-12



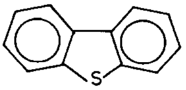
2-13



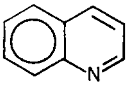
2-14



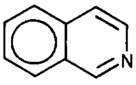
2-15



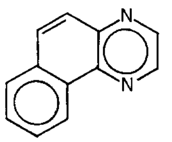
2-16



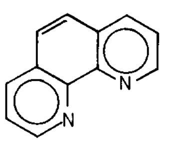
2-17



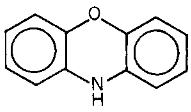
2-18



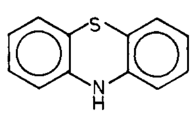
2-19



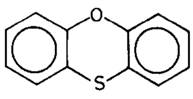
2-20



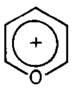
2-21



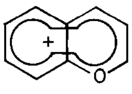
2-22



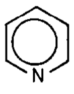
2-23



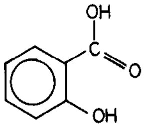
2-24



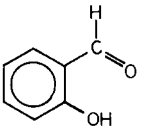
2-25



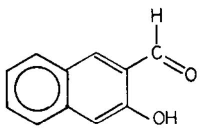
2-26



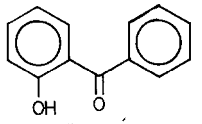
3-1



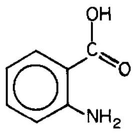
3-2



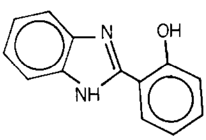
3-3



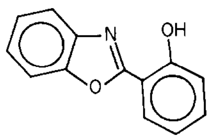
3-4



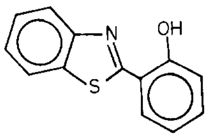
3-5



3-6



3-7



3-8

3. QUANTUM CHEMICAL METHOD

Recently Fratev *et al.* succeeded in calculation the fluorescence spectra of a large series of conjugated hydrocarbons and related compounds.[1,12] The method used in this paper is similar to Fratev's procedure. For the sake of simplicity only one parameter set for the calculation of absorption and fluorescence spectra has been used. This set, calibrated for giving a good description of absorption maxima and checked earlier[13] is a little different from that of Fratev *et al.*

Starting from ordinary PPP calculations, the geometry of the first excited singlet state has been corrected by using the bond orders $p^*_{\mu\nu}$ of this state in an iterative way. The relation between $p^*_{\mu\nu}$ and the distance $R^*_{\mu\nu}$ is given by:

$$R^*_{\mu\nu} = a - bp^*_{\mu\nu}. \qquad (6)$$

On the other hand $R^*_{\mu\nu}$ is connected with the resonance integrals $\beta_{\mu\nu}$ in the PPP-equations

$$\beta_{\mu\nu} = \beta^0_{\mu\nu} \exp\left[-2.3\ (R^*_{\mu\nu} - R^0_{\mu\nu})\right]$$

which are the input values for the next iteration step.[14] It has been found that a correction of the $\gamma_{\mu\nu}$-integrals by the corrected $R^*_{\mu\nu}$-values has no considerable influence on the transition energies and can be omitted. The values of a in eqn (6) were 1.517, 1.451, 1.410 Å for CC–, CN- and CO– bonds, respectively.[15] The constant b has been assumed to be 0.18 in all cases. For $R^0_{\mu\nu}$ in eqn (7) a rough value of 1.40 Å seems to be reliable. All monoexcited configurations have been taken into account. The convergence of this SCF-SC (β^*)-LCI-method is rather streamlined: only 3–5 iteration steps were necessary to obtain self-consistent transition energies.

4. RESULTS AND DISCUSSION

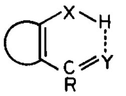
In Table 1 the energy differences between the geometrically relaxed ground state[a] and a nonrelaxed excited singlet state (corresponding to a vertical transition observable in the absorption spectrum) and between a geometrically relaxed excited singlet state and a nonrelaxed ground state (corresponding to a vertical transition observable in the fluorescence spectrum) expressed by the wave numbers are collected and compared with the experimental data as far as available.

The good agreement between the vertical energies obtained in the PPP-method and the positions of maxima of the longest wavelength UV absorption band is very well known and should not be discussed here.[13] We find, however, also a fair agreement between the energies of the geometrically relaxed excited states and the fluorescence maxima, supporting Fratev's results in a more extended way. Figure 1 shows the good agreement in the overall description of absorption and fluorescence spectra for six typical cases.

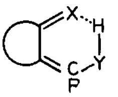
In Fig. 2 finally a statistical correlation between the wave numbers of maxima of the geometrically relaxed π-systems and the maxima of the fluorescence band has been made. The diagram shows a significant relation between these two amounts and suggests that the method applied should reproduce the absorption and fluorescence maxima of any conjugated system.

Special attention will be focused to the good reproduction of the fluorescence spectrum of NPU (1–7) by the method applied, for this compound will be the key for our further investigations (cf Part II).

For the compounds summarized in group **3** an anomalous Stokes shift due to a photoprototropy has been postulated.[22,24] It is interesting that a good agreement of the calculated transition energies with the anomalously shifted fluorescence bands could be reached. To realize that, first the vertical transition of the prototropic form **2** has been calculated.



1



2

An usual PPP-calculation of this structure provides a considerable red shift of the transition energy in

---

[a] All geometrical relaxation movements combined with a change of either bond or dihedral angles are excluded in our consideration.

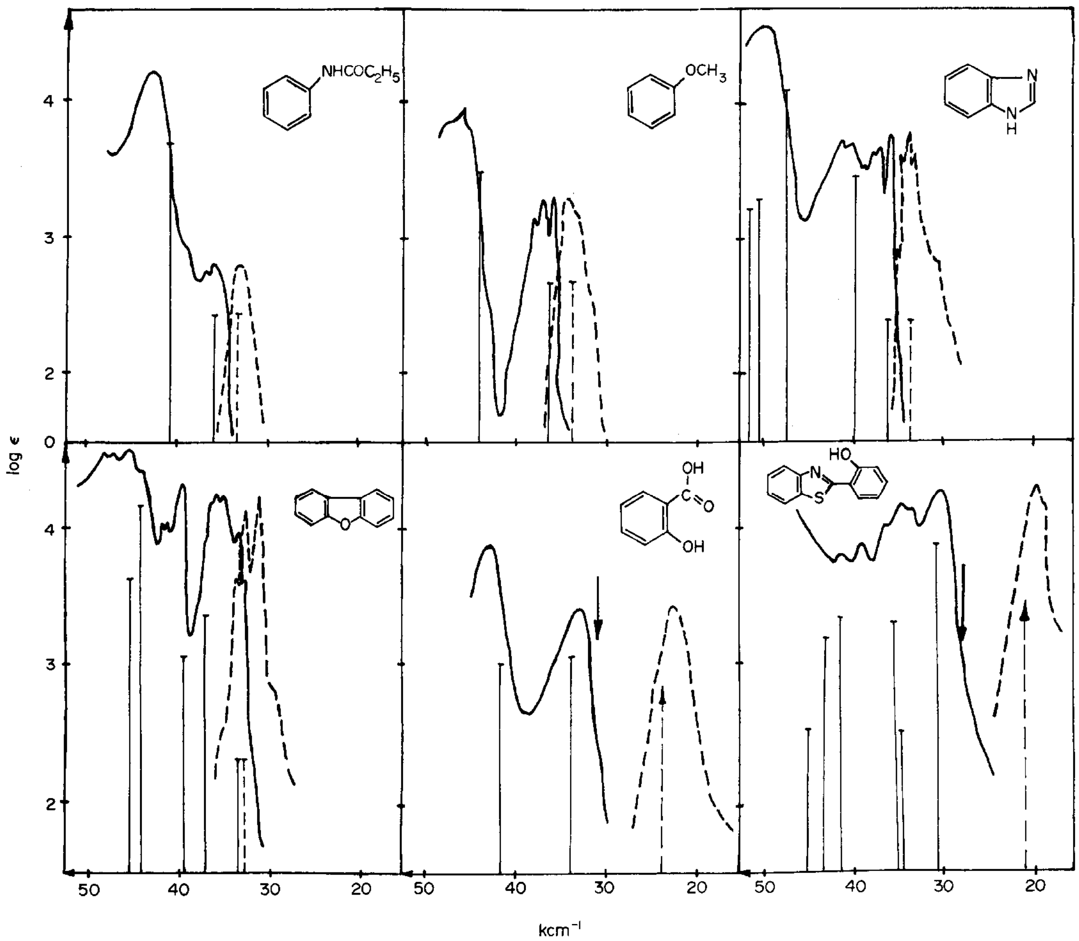


Fig. 1. Spectral curves of absorption and fluorescence and theoretical transition energies for some selected examples of the compounds considered. (The length of the transition lines is in proportionality to the theoretical oscillator strengths. The short arrows show the calculated positions of the "normal" fluorescence in the case of photoprototropic systems. For the occurrence of the latter there are some hints for 3-1,[22] 3-7 and 3-8.[35])

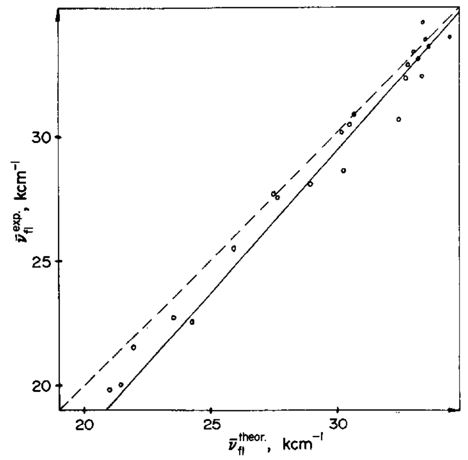


Fig. 2. Correlation between the maxima of the fluorescence spectra and the vertical transition energies from the geometrically relaxed excited singlet state to the ground state. (The dashed line represents the function y = x for comparison.)

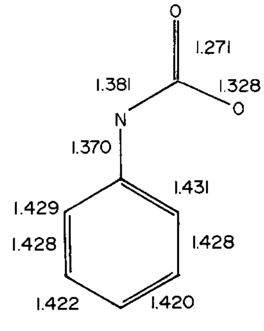


Fig. 3. Bond lengths in Å of NPU in the first excited singlet state.

comparison to **1**. Applying eqns (6) and (7) the "normal" Stokes-shift of **2**, which corresponds to the anomalous Stokes-shift of **1** could be obtained.

It can be seen that practically each compound of the type **3** should have a fluorescence spectrum of the prototropic form **2**, as the fluorescence spectrum of the structure **1** in nearly all cases should be positioned at energies considerably higher and in disagreement with the actual position of the fluorescence band.[b]

---

[b] cf footnote in Fig. 1.

Table 1. Comparison of the calculated wave numbers in kcm^{-1} and oscillator strengths for the low energetic absorption and fluorescence transitions and the corresponding experimental values of the compounds treated

	theoretical			experimental			
Compound	$\tilde{\nu}_{fl}$	(lgf)	$\tilde{\nu}_{abs}$ (lgf)	$\tilde{\nu}_{fl}$	Ref.	ν_{abs}	Ref.
1-1	35.7[a]	(forb.)	38.4 (forb.)	35.6	16	38.4	25
1-2	34.6[a]	(− 1.78)	36.9 (− 1.56)	33.8	16	36.0	25
1-3	33.6	(− 1.46)	35.8 (− 1.32)	34.4	16	36.0	25
1-4	35.4	(− 2.88)	38.0 (− 2.66)	—[b]		37.8	25
1-5	33.2[a]	(− 1.43)	35.2 (− 1.31)	30.6	17	35.6	25
1-6	33.5	(− 1.85)	36.1 (− 1.70)	32.2	10	35.5	26
1-7	33.8	(− 1.74)	35.9 (− 1.59)	33.4	10	35.8	27
2-1	42.7	(− 1.43)	47.3 (− 1.46)	—[b]		48.1	25
2-2	43.3	(− 1.97)	48.3 (− 2.01)	—[b]		48.3	25
2-3	41.4	(− 0.83)	43.7 (− 0.77)	—[b]		43.3	25
2-4	41.5	(− 0.69)	46.6 (− 0.69)	—[b]		48.5	25
2-5	41.3	(− 0.58)	46.6 (− 0.57)	—[b]		48.8	25
2-6	39.0	(− 0.60)	42.5 (− 0.58)	—[b]		43.1	25
2-7	33.4	(− 1.74)	35.6 (− 1.61)	33.9	18	34.8	25
2-8	33.8	(− 2.19)	36.0 (− 2.17)	—[b]		35.6	25
2-9	33.0	(− 1.38)	34.6 (− 1.13)	—[b]		33.6	25
2-10	33.7	(− 1.71)	36.0 (− 1.66)	33.0	18	36.0	25
2-11	33.9	(− 1.74)	36.2 (− 1.59)	—[b]		36.1	25
2-12	33.3	(− 1.57)	35.0 (− 1.40)	—[b]		35.3	25
2-13	33.2	(− 1.24)	35.6 (− 1.18)	33.2	18	36.3	25
2-14	30.4	(− 1.44)	32.4 (− 1.36)	28.5	18	30.9	25
2-15	33.0	(− 1.82)	33.6 (− 1.68)	32.7	19	34.8	25
2-16	30.3	(− 1.26)	31.6 (− 1.21)	30.1	19	30.6	25
2-17	30.8	(− 1.55)	32.5 (− 1.51)	31.2	19	31.9	25
2-18	30.6	(− 1.52)	32.3 (− 1.28)	30.6	20	31.5	25
2-19	27.7	(− 0.81)	29.5 (− 0.707)	27.5	21	27.8	21
2-20	29.0	(− 3.15)	30.6 (− 3.50)	28.0	21	30.9	25
2-21	27.6	(− 1.30)	28.9 (− 1.64)	27.6	15	31.7	25
2-22	26.1	(− 2.04)	28.5 (− 1.72)	25.5	15	31.3	25
2-23	29.0	(− 1.75)	31.0 (− 3.80)	—[b]		33.7	15
2-24	31.2	(− 0.45)	34.1 (− 0.41)	—[b]		36.1	28
2-25	24.7	(− 1.01)	27.8 (− 0.99)	—[b]		27.5	29
2-26	35.6	(− 1.52)	(− 1.48)	—[b]		38.9	25
3-1	24.3[c]	(− 0.40)	33.9 (− 0.94)	22.5	22	32.9	22
3-2	24.5[c]	(− 0.47)	32.9 (− 0.89)	—[b]		31.1	30
3-3	19.1[c]	(− 0.45)	29.4 (− 1.00)	—[b]		28.8	31
3-4	21.4[c]	(− 0.20)	32.3 (− 0.70)	—[b]		29.7	25
3-5	23.5[c]	(− 0.40)	31.2 (− 1.00)	22.7	23	31.1	32
3-6	22.0[c]	(− 0.14)	31.6 (− 0.14)	21.5	24	31.2	33, 35
3-7	21.4[c]	(− 0.16)	31.4 (− 0.12)	20.0	24	31.0	33, 35
3-8	21.1[c]	(− 0.15)	30.5 (− 0.08)	19.8	24	30.2	33

[a] also treated in.[12]

[b] no experimental data available.

[c] calculated for the phototautomeric "cis-keto species".

Concerning the applied method it has been found that the special difficulties in the treatment of heterobonds existing in the variable β-technique are evidently of no influence on the results obtained. Thus, the formulae given by Dehler[15] and by Nishimoto and Forster[34] provide practically the same results concerning the decrease of transition energy due to a geometrical relaxation as it could be obtained by a simple "C–C-approximation" using as well the constants for carbon in eqn (6) for essential single bonds of heteroatoms.

However, the simple "C–C-approximation" provides only qualitative tendencies concerning the change of geometry in the first excited state, whereas the excitation energy in this respect is evidently less sensitive. Therefore, an analysis of the typical changes in the geometry of excited equilibrium states, carried out on the basis of our calculations, should be omitted for sake of brevity. Only the geometry of **1-7** in its lowest excited singlet state, obtained by applying the Nishimoto–Forster formulae[34] will be given (cf Fig. 3). The result of the excitation is a considerable widening of the C–C bonds in the benzene ring as well as the carbonyl bond and a shortening of the nitrogen-ring bond, representing a stronger resonance interaction of the substituent to the ring in the excited state.

The good overall agreement between theoretical and experimental data of absorption and fluorescence spectra encouraged us to connect these results with the energy transfer properties of the treated compounds. This will be done in the following paper.

REFERENCES

[1] F. Fratev, G. Hiebaum and A. Gochev, *J. Mol. Structure* **23**, 437 (1974).

[2] K. Schwetlick, R. Noack and G. Schmieder, *Z. Chem.* **12**, 107 (1972).

[3] K. Schwetlick and R. Noack, *Ibid.* **12**, 109 (1972).

[4] K. Schwetlick and R. Noack, *Ibid.* **12**, 140 (1972); **12**, 143 (1972); **14**, 99 (1974).

[5] R. Noack and K. Schwetlick, *Tetrahedron* **30**, 3799 (1974).

[6] D. Bellus and K. Schaffner, *Helv. chim. Acta* **51**, 221 (1968).

[7] D. J. Trecker, R. S. Foote and C. L. Osborne, *Chem. Commun.* 1034 (1968).

[8] H. C. Beachele and J. L. Chang, *J. Polymer Sci.* Part A-1 **10**, 503 (1972).

[9] H. J. Hagemann, *Rec. Trav. Chim.* **91**, 362 (1972).

[10] J. Stumpe, Dissertation, TU Dresden (1975).

[11] Th. Foerster, *Modern Quantum Chemistry* (Edited by O. Sinanoglu), Vol. III, p. 93, New York (1965).

[12] F. Fratev and A. Tadler, *J. Mol. Structure* **27**, 185 (1975).

[13] cf J. Fabian, A. Mehlhorn and R. Zahradnik, *Theoret. Chim. Acta* **12**, 247 (1968); *J. Phys. Chem.* **72**, 3975 (1968).

[14] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc. London* **78**, 1310 (1961).

[15] H. H. Mantsch and J. Dehler, *Canad. J. Chem.* **47**, 3173 (1969).

[16] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, New York (1971).

[17] V. L. Ermolayev and I. P. Kotljar, *Opt. i Spectr.* **9**, 353 (1960).

[18] H. U. Schütt and H. Zimmermann, *Z. Elektrochem.* **67**, 54 (1963).

[19] J.-M. Bonnier, P. Jardon and J.-P. Blanchi, *Bull. Soc. Chim. Fr* **12**, 4787 (1968).

[20] H. Zimmermann and N. Joop, *Z. Elektrochem.* **65**, 61 (1961).

[21] H. Gropper and F. Dörr, *Ibid.* **67**, 46 (1963).

[22] A. Weller, *Ibid.* **60**, 1144 (1956).

[23] H. O. Albrecht, *Z. physikal. Chem.* **136**, 321 (1928).

[24] D. L. Williams and A. Heller, *J. Phys. Chem.* **74**, 4473 (1970).

[25] UV-Atlas organischer Verbindungen (DMS-Kartei), Bd. 1-5 Weinheim (1966).

[26] H. E. Ungnade and E. Hansbury, *J. Org. Chem.* **17**, 742 (1952).

[27] S. L. Shapiro, I. M. Rose, F. C. Testa, E. Roskin and L. Freedman, *J. Am. Chem. Soc.* **81**, 6498 (1959).

[28] J. Degani, R. Focchi and C. Vinzenzi, *Gazz. Chim. Ital.* **94**, 203 (1964).

[29] J. Degani, R. Focchi and C. Vinzenzi, *Boll. Sci. Fac. chim. ind. Bologna* **23**, 151 (1965).

[30] E. Mayer-Pitsch and H. Troger, *Z. Elektrochem.* **47**, 60 (1941).

[31] H. Fernholz, E. Hartwig and J.-C. Salfeld, *Liebigs Ann.* **B576**, 131 (1952).

[32] H. Dannenberg, *Z. Naturforsch.* **4b**, 327 (1949).

[33] D. Schulz, Diplomarbeit, TU Dresden (1974).

[34] K. Nishimoto and L. S. Forster, *Theoret. Chim. Acta* **3**, 407 (1965).

[35] M. D. Cohen and S. Flavian, *J. Chem. Soc.* 317, 321 (1967).