

DISTANCE MEASURES

A New Tool for the Analysis and the Characterization
of Molecular Properties

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Dedicated to Professor E. Clar on the occasion
of his 80th birthday

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5. LIST OF SYMBOLS

$C = \{C_1, C_2, \dots, C_p\}$	characteristics; p - number of characteristics
$C' = \{C_1, C_2, \dots, C_q\}$	subsets of C
$C'' = \{C_{q+1}, C_{q+2}, \dots, C_p\}$	subsets of C
$C^1, C^2, \dots, C^\delta, \dots, C^\lambda, \dots, C^\epsilon$	subsets of C
$d(X_k, X_1)$	distance function (metric between Q_k and Q_1 with respect to the selected characteristics $\{C_1, C_2, \dots, C_p\}$)
$\bar{d}_r(X_k, X_1)$	Minkowski metric
$d'(X_k^1, X_1^1)$	partial distances between Q_k and Q_1 with respect to C' and C''
$d''(X_k^2, X_1^2)$	partial distances between Q_k and Q_1
$d^1, d^2, \dots, d^\delta, \dots, d^\epsilon$	total distance measure
$\bar{d} = \frac{d}{\sqrt{n}}$	specific distance measure
$d[P^M(I), P^L(J)]$	total distance measure
$d[P^{Mi}(I), P^{Li}(Ji)]$	partial distance measure
$\bar{d}_T = d_T[P_T(I), P_T(O)]$	partial distance measure characterizing el. transition $O \rightarrow I$ for subunit T of molecule $T-U$
$\bar{d}_U = d_U[P_U(I), P_U(O)]$	similarly, for subunit U
$\bar{d} = d[P(I), P(O)]$	total distance characterizing el. transition $O \rightarrow I$ in molecule $T-U$
$\bar{d}_T = \frac{d_T^2}{d^2}$	relativated distances characterizing localization or delocalization or exciton-like excitation, in el. transition $O \rightarrow I$
$\bar{d}_U = \frac{d_U^2}{d^2}$	
$d_T[\Delta P_T(I), \Delta P_{T_0}(I)]$	specific partial distance estimating how similar a transition $O \rightarrow I$ is in a subunit T in $T-U$ to that in the reference unit T_0 , as measured by the change in el. density distribution

$d_U[\Delta P_U(I), \Delta P_{U_0}(I)]$	same, for U in T-U, relative to reference unit U_0
L(J)	many-electron system in arbitrary el. state J, of any multiplicity
$L1(J1), L2(J2), \dots, Li(Ji), \dots$	reference subunits in el. state $J1, J2, \dots, Ji, \dots$ respectively, making up the reference system L
M(I)	many-electron system in arbitrary el. state I, of any multiplicity
$M1(I), M2(I), \dots, Mi(I), \dots$	molecular subunits of M(I)
$n = \sum_i n_i$	number of $P_{\mu\nu}$ elements (considered in formula 2.11)
n_i	number of subcharacteristics $P_{\mu\nu}^{Mi}(I)$, or $P_{\mu\nu}^{Li}(Ji)$ respectively
n_T, n_U	number of $P_{\mu\nu}$ elements in the subunits T, U
P	charge - bond order matrix
$P_{\mu\nu}$	elements of charge - bond order matrix
$P^M(I)$	charge - bond order matrices of a molecular system M and the reference system L, in el. states I and J, respectively
$P^L(J)$	
$P_{\mu\nu}^{Mi}(I)$	elements of the submatrix $P^{Mi}(I)$ of the total matrix $P^M(I)$
$P_{\mu\nu}^{Li}(Ji)$	elements of the submatrix $P^{Li}(Ji)$ of the total matrix $P^L(J)$
$P^{Li}(Ji)$	charge - bond order matrix of the reference unit $Li(Ji)$
$\Delta P(I) = P(I) - P(O)$	matrix characterizing the change in el. density distribution upon excitation from ground (O) to excited state (I), in molecule T-U

$\Delta P_O(I) = P_O(I) - P_O(O)$	matrix characterizing the change in el. density distribution upon excitation from ground (O) to excited state (I), for reference system T_O, U_O
$\Delta P_{T_O}(I), \Delta P_{U_O}(I)$	same, for molecular subunit T_O , respectively U_O
$Q = \{Q_1, Q_2, \dots, Q_m\}$	objects; m = number of objects
$s(X_k, X_1)$	similarity between Q_k and Q_1 with respect to the selected characteristics $\{C_1, C_2, \dots, C_p\}$
$s^\delta \equiv s(d^\alpha \delta)$	measure of partial similarity (abbreviation)
$(T-U)(I)$	molecular system M(I) composed from two molecular subunits T and U
T_O, U_O	reference system of uncoupled molecular subunits T_O and U_O
$T_O(JT)$	reference units corresponding to $(T-U)(I)$ in states JT and JU, respectively
$U_O(JU)$	
$X = \{X_1, X_2, \dots, X_m\}$	
$X_1 = (X_{k1})$	p x 1 dimensional vector characterizing Q_1
X_{k1}	value of k-th characteristic of object Q_1
$X'_k = (X_{1k}, X_{2k}, \dots, X_{qk}, 0, 0, \dots, 0)$	
$X''_k = (0, 0, \dots, 0, X_{(q+1)k}, X_{(q+2)k}, \dots, X_{pk})$	
(blank)	neutral molecule
+	cation
-	anion
.	radical
+. .	cation-radical
-. .	anion-radical

1. THE EMBEDDING OF DISTANCE MEASURES INTO THE FIELD OF
CONCEPTUAL QUANTUM CHEMISTRY

In the last decade quantum chemical papers in the literature have increased both in number and variety. If one considers this development from the viewpoint of experimental chemists, since their work is aimed to be supported and inspired by quantum chemistry, three main directions become recognizable:

The first group of papers deals with the advancement of quantum mechanical theory and methodology. Extended basis sets are tested and new mathematical approaches for solving specific details of the eigenvalue problem are revealed. In spite of the importance of these papers to further the field of quantum chemistry the chemist inclines to ignore them, considering purely theoretical investigations as quasi-independent of his own work.

The second group of papers aims to reproduce experimental results by means of quantum chemical standard techniques which are tractable and feasible enough to be used as routine procedures in computer programs. The most important aspect of these computerized methods is their applicability to a large number of different molecules. The content of these papers consists therefore mostly in comparisons of some physical or chemical properties, with the corresponding theoretical values, for a small number of different compounds often related to each other. The extent of agreement is frequently used to evaluate scope and capacity of the method. The problems to reproduce physical observables numerically are rather large since even modern quantum chemical methods provide only incomplete description of complex experimental situations and events. Consequently, the

relations between quantum chemical and experimental results are either of indirect character, or numerical congruence is achieved by semiempirical adaptations of certain quantum mechanical integrals. The deficiencies of the quantum chemical model frequently prevent a realistic evaluation of agreement or discrepancy between theory and experiment.

There is no doubt that this kind of quantum chemical papers is watched with some scepticism and even mistrust by experimental chemists, and their reputation seems to be lower than the scientific value of most of them. The reason for the chemist's preconceptions consists in the fact that a purely numerical reproduction of preceding experiments is interpreted as a bare plagiarism not able to inspire further experimental work. However, it should not be overseen that each modern experimentalist will appreciate papers which connect numerical reproduction of known experimental values with their extrapolation and prediction of unknown ones.

The pure production of numbers in ab initio quantum chemistry reveals also an essential difference in the way of thinking between the "pure" quantum chemist and the chemical experimentalist: Quantum chemical calculations of molecular properties are always restricted to a small number of molecular systems. The transferability of the results to other systems is rarely possible. The aim of such investigations is necessarily specific. In contrast, the experimental chemist is mostly interested in investigations of conceptual character.

This is the origin of a third group of quantum chemical papers which have become very popular in chemistry. The aim of these

studies is not so much the numerical reproduction of specific molecular properties but rather the outline of qualitative trends in order to stimulate experimental chemists to new conceptual insights.

There is one group of trend informations arising from simplified quantum chemical models where the numerical results are mainly determined by the topology of the molecules under study. Such approximative calculations do not reproduce well the experimental values but they elucidate the physical relations between them. This situation is typical for the simple Hückel formalism including low order perturbation theory [1], as well as for analytic formulae derived graphtheoretically [2] which produce Hückel numbers and expansion coefficients for classes of topologically related compounds (e.g. homologue series). Along this line, qualitative changes of orbital energies and one electron wave function as a consequence of structural modifications become the major aim of the investigations. A further property of the wave functions, their symmetry, is the basis of the Woodward-Hoffmann-rules [3] and gives rise to the most convincing proof of the useability of quantum chemistry for understanding and systematizing complicated experimental results. Closely related to these rules is the correlation of initial and final states in the course of chemical reactions, whereby global or local symmetry characteristics are taken into account [4]. State correlations permit a qualitatively new and elegant classification and treatment of thermal and photochemical reactions [5].

A second alternative in the field of conceptual quantum chemistry is the secondary mathematical processing of numerical

results obtained by more sophisticated quantum chemical methods in order to condense the embarrassing variety of numbers to well defined indices suited for supporting, correcting and even creating new chemical models.

Based on the analogy principle, the mental breakdown of larger molecules into molecular sub-units or, inversely, the mental composition of the molecule from these sub-units (or building blocks), is one of the most important concepts able to stimulate the chemist's intuition. This can be demonstrated by several examples from chemical history: the model of the two-centre bond [6], the chromophore concept [7] and, more specifically, the polymethine concept [8,9] in dye-stuff chemistry and also the model of aromatic π -electron sextets in polycondensed benzenoid hydrocarbons [10].

Thus, the secondary processing of quantum chemical results aims to reveal two-atomic or polyatomic molecular sub-units in larger molecules, the extent of coupling of these sub-units to each other and the relationships between the molecular properties of the total system and those of the sub-units.

There are many successful attempts along this line. Accepting certain approximations, the total energy of a molecular system can be partitioned into energetic contributions of atoms and two-centre bonds and this provides information about bond strengths [11]. In the same way, delocalized MO's can be analyzed with respect to local electron distributions, such as electron density on atoms and in bonds (population analysis [12]) or the MO's can be transformed into localized two-centre orbitals via a unitary transformation [13].

Furthermore, the mental decomposition of molecules into multi-atomic sub-units has been found very useful for special purposes. Thus, Clar's idea that the π electron sextet of a single benzene sub-unit should be differently evolved depending on its topological position within a polycyclic benzenoid compound, has been theoretically founded by the character orders [14]. The detection of a multiatomic sub-unit within a more complex system becomes possible by mathematically implementing comparisons of the electronic structure of the sub-unit (e.g. benzene, butadiene) and the electronic structure of the respective reference system. In a development of the Pars Orbital theory, the sub-unit can be in an arbitrary electron state, but the reference system is always in the ground state [15].

From a mathematical point of view, character orders are obtained by the projection of the wave function of the reference molecule onto the wavefunction of the molecule considered.

The Configuration analysis proposed by Baba et al. [16] is based on rather similar ideas. This interpretative analysis can be performed for both the ground and excited states of π -conjugated systems and had been used originally for a descriptive interpretation of the u.v. spectra of monosubstituted benzenes. Recently, the method encountered broad application for describing and interpreting the electronic spectra of organic conjugated molecules of various kinds, particularly of organic colorants [17].

The Configuration analysis provides criteria for the best fit decomposition of ground state systems into "no bond" sub-units; here the results are comparable with those obtained by the use of character orders. Moreover, based on CI wave functions, information

about the character of excited states in terms of sub-units becomes available as well. Starting from molecular sub-units, excited states can be classified as locally excited states (excitation more or less restricted to one sub-unit), exciton-like excited states (delocalized excitation of weakly coupled sub-units) and intramolecular charge transfer excited states (charge transfer from one sub-unit to the other one as a consequence of excitation) [18]. Analyses of this kind enable the spectroscopist to understand clearly and descriptively the u.v. spectra of conjugated systems [19]. Finally, configuration analysis permits state correlation by comparing electronic states of iso-electronic systems where no decomposition is necessary.

In spite of all advantages, projecting techniques have some serious drawbacks as a consequence of their mathematical formalism. Without difficulties they may be applied to π -MO-systems since in that case a proper decomposition into sub-units may be performed. Difficulties arises when complete electronic structures are considered since there are some hydrogen atoms in the reference compounds but not in the molecule decomposed [20]. This holds for both configuration analysis and character orders. Moreover, in configuration analysis the quality criterion for a certain projection depends strongly on the width of configuration interaction. A large number of configurations contracts the range of the projection criterion values, as the total system becomes increasingly better describable in terms of sub-units. It is also well-nigh impossible to project wave functions of different multiplicity onto each other. The configuration analysis of a closed shell system requires closed shell sub-units. In this way some

specific schemes of decomposition cannot be carried out.

All these difficulties do not appear in the distance/similarity measure approach [21] which is based on the calculation of the distance between two matrices [22] reflecting essential features of the two molecular systems compared. As examples for such matrices may serve those which represent the distribution of electron energy, and the distribution of electron density, over atoms and bonds. This method [21] allows to compare systems in arbitrary electronic states and it could be applied in the framework of any LCAO-MO approximation independently from the basis set used.

In this paper the use of the Euclidean distance between two one-particle density matrices, P , is reviewed. The analysis of the P -matrices instead of the state wave functions turns out favourably, since modifications of the Hamiltonian, variation of the basis set and of the state multiplicity affect only the numerical values of the P -matrix elements but not their number. Therefore, the procedure can be applied to any electronic state of arbitrary multiplicity.

In recent years distance and similarity measures have been applied to various fields [23-29]. In these papers, however, slightly different definitions were used and the numerical data are scattered in the literature.

The present paper has therefore the aims:

- i) to unify the definitions given for distance measures;
- ii) to review the applicative possibilities disclosed until now by inclusion of numerous examples;
- iii) to incorporate distance measures into interpretative quantum chemistry and to compare them with alternative approaches.

2. DERIVATION AND PHYSICAL FOUNDATION OF DIFFERENT DISTANCE MEASURES

2.1 THE CONCEPT OF SIMILARITY (DISTANCE) AND THE PRINCIPLE OF ANALOGY IN CHEMISTRY

In chemistry, a similarity between the essential characteristics of two molecules allows the investigator to make certain assumptions about the chemical and physical properties of one of the molecules if those of the other are known. For example, the similarity between the benzeneoid molecular subsystem (fragment) of polycyclic aromatic hydrocarbons and the benzene molecule allowed Clar [10] to put forward his well-known classification of these compounds. This is the essence of the "principle of analogy", long used intuitively by chemists in the formulation of classes of compounds from the so-called "parent" compounds and their derivatives, as well as in the application of established routes to the synthesis of new compounds, etc.

In recent years, the concept of similarity has become increasingly quantified in chemistry with the help of statistical techniques. Using computers to process banks of experimental data, various attempts have been made to correlate these data with a wide variety of chemical and physical properties [22,30-32].

In the present chapter we shall define the distance/similarity measures with respect to quantum chemical characteristics. An essential characteristic of all molecules (many-electron systems) is their electron distribution, which in quantum chemistry is described by the one-electron density function; in the LCAO approximation this function is represented by the charge-bond order matrix, P . The elements of the P -matrix reflect

the electronic structure of molecules in a precise way, and therefore they are often used in the description of molecules, e.g. in molecular diagrams [33]. Hence, when we refer later to molecular electronic structure, we have in mind the elements of the charge-bond order matrix.

On the other hand, we introduce the mathematical concept of distance and similarity measures into quantum chemistry to provide an estimate of the difference and similarity, respectively, between two many-electron systems in arbitrary electronic states with respect to their electronic structure. As will be seen below, the proposed method can be applied, in principle, within the framework of any quantum-chemical LCAO approximation.

2.2 MATHEMATICAL FORMALISM

Let the set $Q = \{Q_1, Q_2, \dots, Q_m\}$ denote m objects (individuals). We shall assume that there exists a set of features or characteristics $C = \{C_1, C_2, \dots, C_p\}$ which are possessed by each object in Q and which can be measured or calculated. We denote the value of the k -th characteristic, C_k , of the object Q_1 by the symbol X_{k1} . For the sake of simplicity it is assumed that X_{k1} do not represent tensors, but only simple numbers. Let $X_1 = (X_{k1})$ denote the $p \times 1$ vector characterizing the object Q_1 . Hence for all objects in Q we have available a set of vectors $X = \{X_1, X_2, \dots, X_m\}$:

	Q	Q_1	Q_2	$\dots\dots\dots$	Q_m	
X	x_1	x_2	$\dots\dots\dots$	x_m		
C_1	x_{11}	x_{12}	$\dots\dots\dots$	x_{1m}		
C_2	x_{21}	x_{22}	$\dots\dots\dots$	x_{2m}		
\vdots	\vdots	\vdots	\vdots	\vdots		
\vdots	\vdots	\vdots	\vdots	\vdots		
\vdots	\vdots	\vdots	\vdots	\vdots		
C_p	x_{p1}	x_{p2}	$\dots\dots\dots$	x_{pm}		

(2.1)

The set X can be thought of as m points in p -dimensional Euclidean space. The relation between two objects, Q_k and Q_l , of Q can be expressed by a distance function (metric) $d(X_k, X_l) \geq 0$ (see, for instance [22]). The value of $d(X_k, X_l)$ for specified X_k and X_l is said to be the distance between Q_k and Q_l with respect to the selected characteristics $\{C_1, C_2, \dots, C_p\}$.

One of the most general forms of the distance d is the Minkowski metric, d_r ,

$$d_r(X_k, X_l) = \left[\sum_{i=1}^p |X_{ik} - X_{il}|^r \right]^{1/r} = |X_k - X_l| \quad (2.2)$$

where $r=1, 2, 3, \dots$; when $r=2$ we obtain the familiar Euclidean metric. Since the mathematical formalism described below is valid for any natural number r , the index r is omitted.

Complementary to the notion of distance is the idea of similarity $s(X_k, X_l)$ between two objects Q_k and Q_l with respect to the selected set of characteristics, $\{C_1, C_2, \dots, C_p\}$.

A non-negative real-valued function, $s(X_k, X_l)$, is said to be a similarity measure [22] if

- a) $0 < s(X_k, X_1) \leq 1$ for $X_k \neq X_1$
 b) $s(X_k, X_k) = 1$ (2.3)
 c) $s(X_k, X_1) = s(X_1, X_k)$

It is important to note that the distance measure d can be used to construct a similarity measure s , or d can itself be used as a similarity measure, always bearing in mind that large distance is equivalent to low similarity and vice versa. Thus, if one prefers to work with similarities rather than distances, a special form of s as a function of d may be selected, satisfying the following conditions:

$$s(d \rightarrow \infty) \rightarrow 0$$

$$s(d = 0) = 1$$

In order to apply this formalism to quantum chemistry it is necessary to formulate some additional properties of the d and s functions. Until now we considered the objects Q_k and Q_1 with respect to the whole set of characteristics $C = \{C_1, C_2, \dots, C_p\}$ and $X_k = (X_{1k} X_{2k} \dots X_{pk})$ and $X_1 = (X_{11} X_{21} \dots X_{p1})$. Let us partition the set C into two disjoint subsets of characteristics, $C' = \{C_1, C_2, \dots, C_q\}$ and $C'' = \{C_{q+1}, C_{q+2}, \dots, C_p\}$; $C = C' \cup C''$ and $C' \cap C'' = \emptyset$. Then X_k and X_1 can be represented as the sum

$$X_k = X_k' + X_k'' \text{ and } X_1 = X_1' + X_1'', \text{ where}$$

$$X_k' = (X_{1k} X_{2k} \dots X_{qk} \ 0 \ 0 \ \dots \ 0)$$

$$X_k'' = (0 \ 0 \ \dots \ 0 \ X_{(q+1)k} X_{(q+2)k} \ \dots \ X_{pk})$$

and similarly for X_1' and X_1'' .

We denote the partial distance between the objects Q_k and Q_1 with respect to C' and C'' by $d'(X_k', X_1')$ and $d''(X_k'', X_1'')$, res-

pectively; eqn. (2.2) holds correspondingly for $d' = |X'_k - X'_1|$ and $d'' = |X''_k - X''_1|$. Using the triangular inequality we obtain

$$|X_k - X_1| = |(X'_k - X'_1) + (X''_k - X''_1)| \leq (|X'_k - X'_1| + |X''_k - X''_1|)$$

i. e. (2.4)

$$d \leq (d' + d'')$$

It is obvious that if we partition the set C into an arbitrary number of disjoint subsets, $C^1, C^2, \dots, C^\delta, \dots, C^\lambda, \dots, C^\epsilon$, for which $\bigcup_{\delta=1}^{\epsilon} C^\delta = C$ and $C^\lambda \cap C^\delta = \emptyset$ for all pairs (λ, δ) , then the following inequality holds

$$d \leq \sum_{\delta=1}^{\epsilon} d^\delta \tag{2.5}$$

In other words, the distance between two objects Q_k and Q_1 with respect to the whole set C is always less than or equal to the sum of the partial distances d^δ between the objects defined with respect to some of their characteristics C^δ .

It also follows from (2.2) that

$$d^\delta \leq d \quad \text{for any } \delta. \tag{2.6}$$

For physical and chemical applications the measure of similarity $s = s(d)$ should necessarily be single-valued and monotonically decreasing from 1 to 0 when the argument d increases from 0 to ∞ . If we denote by $d(1)$ and $d(2)$ any two values of d, and if $d(1) \leq d(2)$

$$\text{then } s(1) \geq s(2) \tag{2.7}$$

Let $d^1, d^2, \dots, d^\delta, \dots, d^\epsilon$ denote the partial distances between the objects Q_k and Q_1 , arranged in increasing order of their values, $d^1 \leq d^2 \leq \dots \leq d^\delta \leq \dots \leq d^\epsilon$. From (2.6) and (2.7), we obtain

$$s(d^1) \geq s(d^2) \geq \dots \geq s(d^E) \geq s(d) \quad (2.8)$$

We shall denote the quantity $s(d^\delta)$ simply by s^δ and shall call it a measure of the partial similarity between Q_k and Q_l determined with respect to a selected subset C^δ of C . Thus the total similarity s between the objects Q_k and Q_l determined with respect to the whole set of characteristics, C , is always less than or equal to the smallest of the partial similarities s^δ , i.e.

$$s \leq \min(s^1, s^2, \dots, s^\delta, \dots, s^E) \quad (2.9)$$

2.3 APPLICATION OF THE FORMALISM FOR THE QUANTUM CHEMISTRY OF MOLECULES

2.3.1 SPECIFICATION OF THE OBJECTS, Q , THE CHARACTERISTICS, C , AND THE VECTORS, X

As discussed in chapter 2.1, we have introduced the distance and similarity measures to compare two many-electron systems, M and L , in arbitrary electronic states, I and J , respectively, of any multiplicity. This means that we identify $M(I)$ and $L(J)$ as members of

$$Q = \{M(0), M(1), \dots, M(I), \dots; L(0), L(1), \dots, L(J), \dots\} \quad (2.10)$$

Comparison may be carried out between a molecular system M in state I and its corresponding reference system L in state J . As discussed below in subsection 2.3.4, L may consist of one or more than one molecules; in the first case J denotes a single quantum number, in the last case an appropriate set of quantum numbers. In general $M \neq L$ and $I \neq J$, but it is also possible to put $M = L$ and/or $I = J$.

The electronic states of many-electron systems can be characterized to some extent by means of their energy, electronic structure and any other measurable or calculable quantities which represent the characteristics C of the objects Q . In most quantum-chemical methods these characteristics are represented by matrices, e.g. the matrix representing the distribution of the electron energy over and between the AO's (in EHT, PPP, CNDO and other methods) [34], the charge-bond order matrix, etc. The elements of these matrices we shall call the subcharacteristics of the object concerned. We apply the formalism described for the characteristics in the previous section now to the subcharacteristics. This means that we use the actual values of the subcharacteristics to construct the vectors X_k and X_l ; it is obvious that the ordering of the elements in both vectors must be of the same type.

In order to compare chemical objects with respect to their electronic structure, the elements of the charge-bond order matrix, $P_{\mu\nu}$, are used as the set of subcharacteristics. Therefore, the vectors X_k and X_l contain the actual values of the elements of the charge-bond order matrices, $P^M(I)$ and $P^L(J)$, of the molecular system M and the reference system L in the electronic states I and J , respectively. These elements reflect the electronic structure of the many-electron systems in a definite way. Since the charge-bond order matrices can be calculated in the framework of any LCAO method for each electronic state, the approach proposed here is applicable to any LCAO-MO method.

2.3.2 DISTANCE MEASURE AND SPECIFIC DISTANCE MEASURE WITH RESPECT TO THE ELECTRONIC STRUCTURE

Having specified the objects, subcharacteristics, and vectors, we can now define the distance and similarity between $M(I)$ and $L(J)$ with respect to their electronic structures.

According to eqn. (2.2), we obtain

$$d_r [P^M(I), P^L(J)] = \left[\sum_{\mu, \nu} |P_{\mu\nu}^M(I) - P_{\mu\nu}^L(J)|^r \right]^{1/r} \quad (2.11)$$

and $s_r = s(d_r)$ should be a single-valued and monotonically decreasing function.

From a mathematical point of view distance norms are equivalent; however, the distances calculated for different $r=1,2,3,\dots$ are quite different, $d_r > d_{r+1}$ [22]. In analogy to other approaches [22,30-32] we use the familiar Euclidean distance, d_2 , denoted simply by d .

From (2.11) it is easily seen that d depends on the number of the elements $P_{\mu\nu}$, i.e. on the size of the considered molecular systems M and L . To eliminate this dependency (or at least to weaken it) we introduce the so-called specific distance measure

$$\bar{d} = d/\sqrt{n} \quad (2.12)$$

where n is the number of $P_{\mu\nu}$ elements considered in (2.11). Since furthermore we shall treat only specific Euclidean distance measures, and, hence, no confusion with total distances can occur, we shall simply denote the specific distance measure by d .

Thus (2.11) takes the form

$$d [P^M(I), P^L(J)] = \left\{ \frac{1}{n} \sum_{\mu, \nu} [P_{\mu\nu}^M(I) - P_{\mu\nu}^L(J)]^2 \right\}^{1/2} \quad (2.13)$$

From a mathematical viewpoint the so defined specific distance measure is identical with the quantity "root mean square" frequently used in statistics, especially in its applications to physics.

Fully analogously to (2.13), one can formulate a specific partial distance measure defined for a given number, n_i , of subcharacteristics $P_{\mu\nu}^{Mi}(I)$ and $P_{\mu\nu}^{Li}(J)$, respectively. The elements $P_{\mu\nu}^{Mi}(I)$ and $P_{\mu\nu}^{Li}(J)$ form the submatrices $P^{Mi}(I)$ and $P^{Li}(J)$ of the total charge-bond order matrices $P^M(I)$ and $P^L(J)$. The submatrices $P^{Mi}(I)$ and $P^{Li}(J)$ represent the electron distribution in definite regions of the molecular system M (in the molecular subunit M_i) and of the reference system L (in the reference subunit L_i) in given electronic states I and J, respectively.

$$d_i = d[P^{Mi}(I), P^{Li}(J)] = \left\{ \frac{1}{n_i} \sum_{\mu, \nu \in Mi(Li)} [P_{\mu\nu}^{Mi}(I) - P_{\mu\nu}^{Li}(J)]^2 \right\}^{1/2} \quad (2.14)$$

In other words, d_i is a distance measure between the subunit M_i and the reference subunit L_i relative to their electronic structure.

It is easy to show that the total specific distance d is expressed through the partial specific distance measures by the relation

$$d = \left[\frac{1}{n} \sum_i n_i d_i^2 \right]^{1/2} \quad (2.15)$$

where $n = \sum_i n_i$.

2.3.3 CHOOSING A SUITABLE ANALYTICAL FORM FOR $s(d)$

Any single-valued and monotonically-decreasing function of

d obeying eqn. (2.3) could serve as a similarity measure. For instance

$$s = [1 + d]^{-1} \quad (2.16)$$

as it is shown in [24] and the references therein.

Another possibility is demonstrated in [25-29]. Since relatively small distances should correspond to high similarity measures, medium distances to medium similarity measures, and finally relatively great distances to relatively low similarity measures, it seems reasonable to choose a bell-shaped curve to represent the function $s(d)$. Of all possible functions of this type we arbitrarily choose the Gaussian [21]

$$s(d) = \exp(-\alpha d^2) \quad (2.17)$$

The choice of a Euclidean metric and the special form (2.17) leads to a simple relation between the partial and total similarity measures, defined by means of specific distances.

$$s(d_i) = \exp(-\alpha d_i^2) \quad (2.18)$$

$$d^2 = \frac{1}{n} \sum_i n_i d_i^2 \quad (2.19)$$

The substitution of (2.18) and (2.19) into (2.17) leads to

$$s(d) = \exp\left[-\frac{\alpha}{n} \sum_i n_i d_i^2\right] = \prod_i \exp[-\alpha d_i^2]^{n_i/n} = \prod_i s_i^{n_i/n} \quad (2.20)$$

The use of the similarity measure, which is defined in the range [0,1], offers more clarity for the quantitative interpretation of the principle of analogy in chemistry. This advantage, however, is greatly weakened by the impossibility of an unequivocal transformation of d into s . Because of this henceforth we shall always use the specific distance measure as the sole

criterion for estimating the similarity between $M(I)$ and $L(J)$ relative to their electronic structure. Of course, as mentioned above, this measure is the reverse of analogy.

2.3.4 CHOOSING THE REFERENCE SYSTEM L

The distance/similarity approach allows great freedom in the choice of the reference system L. We shall consider briefly some of the possible ways in which this may be done.

2.3.4.1 COMPOSITE MODEL

One of the main approaches for choosing the reference system L is based on the so-called "composite model", which is used quite often in structure chemistry, and more specifically, in dye chemistry. Within this model the molecular system (molecule or supermolecule) M in state I is considered as consisting of submolecular units $M_1(I), M_2(I), \dots, M_i(I), \dots$. The electronic structure of each submolecular unit $M_i(I)$ is represented as a diagonal block of the charge-bond order matrix of M.

$$P^M(I) = \left[\begin{array}{c|c|c} & & \\ \hline & P^{M_i}(I) & \\ \hline & & \end{array} \right] \quad (2.21)$$

Within the composite model, a reference system L corresponds to the molecular system M, and L consists of non-inter-

acting "building blocks", which we shall call "reference sub-units"- $L_1, L_2, \dots, L_i, \dots$. They can be electrically neutral molecules, ions, radicals, ion-radicals, and they can be in different electronic states J_i

$$L = \{L_1(J_1), L_2(J_2), \dots, L_i(J_i), \dots\} \quad (2.22)$$

The electronic structure of the reference subunit $L_i(J_i)$ in electronic state J_i is represented by the corresponding charge-bond order matrix $P^{L_i}(J_i)$. Using all the matrices $P^{L_i}(J_i)$ we construct a supermatrix $P^L(J)$ characterizing the electronic structure of the reference system L , where J indicates the set $\{J_i\}$ according to eqn. (2.22).

$$P^L(J) = \begin{bmatrix} & & 0 & & 0 \\ & & | & & | \\ 0 & & P^{L_i}(J_i) & & 0 \\ & & | & & | \\ 0 & & 0 & & \end{bmatrix} \quad (2.23)$$

As can be seen from (2.23), the supermatrix $P^L(J)$ is of block-diagonal form. M and L should always be calculated under similar conditions, i.e. the same quantum chemical approximation, parametrization, basis sets, etc. in order that the matrices P^M and P^L are comparable.

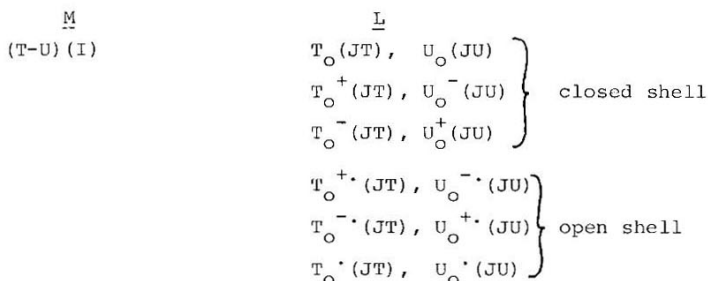
The distance measures (2.13) calculated relative to different reference systems L can give an unequivocal answer to the question of to what extent a molecular system M in state I can be considered to consist of weakly interacting reference units. The minimum-valued distance measure $d[P^M(I), P^L(J)]$ determines that reference system L , which best describes the molecular system $M(I)$ in the framework of the composite model, and is called the "best fit des-

cription".

It is important to note that the best fit description may be completely different for the different electronic states of the molecular system M, i.e. each electronic state of M can be considered in general as consisting of differently structured building blocks (see for instance Section 3.1.3).

In addition, the possibility for every reference unit, L_i , to be in an arbitrary electronic state, J_i allows us to carry out a complete analysis of the electronic states of M, as well as of the electronic transitions in M in terms of the composite model (see Section 3.1 and 3.2). The analysis can use the total distance measure $d[P^M(I), P^L(J)]$ where L corresponds to the best fit description, as well as the measures of partial distances between the electronic structure of the molecular subunit M_i and the reference subunit L_i , i.e. $d[P^{M_i}(I), P^{L_i}(J_i)]$.

An essential advantage of the proposed distance approach is the possibility of comparing the molecular system M in state I not only with reference systems composed of closed-shell reference subunits, but also with reference systems L which are composed from open-shell reference subunits. For example, for a molecule considered as consisting of two molecular subunits T and U, for every state I we can juxtapose the following reference systems composed of reference subunits T_0 and U_0 :



where T_O , T_O^+ , T_O^- , $T_O^{+\cdot}$, $T_O^{-\cdot}$ and T_O^{\cdot} are neutral molecule, ions, ion-radicals and radicals, respectively.

The non-existence of a best fit closed-shell description may indicate either strong interaction between T and U, or that the molecular state (T-U) (I) can be described better within the composite model relative to open shell reference systems. In Section 3.1.4 examples are given where the ground state of T-U may be considered as consisting of two weakly interacting closed shell reference subunits, while the excited states are interpreted as composed of weakly coupled open shell reference subunits. The use of closed shell as well as open shell reference systems is especially important when electronic states are considered in which strong intramolecular charge transfer is involved (see Section 3.1.4).

As will be discussed in Section 4, all projection methods such as the configuration analysis of Baba et al. [16] and the Pars Orbital theory [14] cannot effect comparisons with open shell reference systems, which reduces their interpretation capability to analyse electronic states and electronic transitions.

2.3.4.2 CHOOSING REFERENCE SYSTEM ON THE BASIS OF THE PRINCIPLE OF ANALOGY

There are many instances where we know a priori which molecular subunit M_i and which reference subunit L_i is of interest to be studied. This is the case when experiment has unequivocally demonstrated to us that the chemical or spectroscopic properties of the molecule M are mainly determined by a high similarity of the molecular subunit M_i to the isolated reference subunit L_i . Examples of such a priori choice of the reference system are given in Sections 3.3.2-3.3.4. In this way the "principle of analogy" indicates unambiguously M_i and L_i , and the partial distance measure is a quantitative expression of the analogy. The remaining partial distance measures, as well as the measure of total distance between M and different reference systems L , don't play any role in these cases.

2.3.4.3 THE MOLECULE M IN GROUND STATE AS REFERENCE SYSTEM

To study the change occurring in the electronic structure of a given molecule M upon excitation, we use the molecule itself in its ground state $M(0)$ as the reference system. A quantitative estimate of the change in the electronic structure upon excitation is the specific distance $d[P^M(I), P^M(0)]$.

If we are interested in the change in the electronic structure occurring within a certain subunit of M , say M_i , we choose for a reference system $M_i(0)$ and calculate the partial distance measure $d_i = d[P^{M_i}(I), P^{M_i}(0)]$.

The two distance measures d and d_i can be used for estimating

the localisation of the electronic transitions upon a given molecular subunit M_i (see Section 3.2).

2.3.4.4 THE REFERENCE SYSTEM L - AN ISO ELECTRONIC ANALOGUE OF THE MOLECULE

There are a number of cases when the comparison of the electronic states of the molecule M with those of its isoelectronic analogue L facilitates the classification of the states $M(I)$ (see Section 3.1.1, correlation analysis).

Concluding Section 2.3.4 we would like to state that there are also other ways of selecting reference systems L , depending on the concrete physical or chemical problems studied. Some of these will be described in the different areas of application (see Sections 3.3.1 and 3.3.5).

2.4 SOME REMARKS TO THE QUANTUM CHEMICAL CALCULATIONS

The charge-bond order matrices are calculated using the SCF-CI-PPP method (closed and open shell) with inclusion of all singly-excited configurations (Tamm-Dankoff approximation). The exact parametrisation employed is described in [35,36]. To avoid prejudicing the results by the choice of resonance integrals, we resorted to a $SC_{\beta,\gamma}$ -PPP treatment which has already been described [37].

Since all resonance integrals $\beta_{\mu\nu}$ between non-bonded atoms are taken to be zero in the PPP method, we shall neglect all elements $P_{\mu\nu}$ in P^M (or P^{M_i}) and P^L (or P^{L_i}) for which the atoms μ and ν are not chemically bonded. In addition, when estimating the distance measure between the electronic structure of M and L ,

the non-diagonal elements $P_{\mu\nu} = P_{\nu\mu}$ should not be favoured over the diagonal elements; therefore we assume that $\mu \leq \nu$ when calculating d .

All distance measures given in this paper are multiplied by 10^3 .

3. EXEMPLIFIED APPLICATIONS OF DISTANCE MEASURES

In the last chapter many different kinds of distance measures have been defined. This manifold of different indices $d(I,J)$ results from two reasons: (i) There is a broad scale to adapt the reference system to the specific problem being solved. Thus, the reference system can be either an iso-electronic analogue of the investigated system or it can consist of alternative combinations of uncoupled molecular systems the composition of which leads to the molecule of interest. Finally, the reference molecule can have an even or odd number of electrons (closed or open shell systems). (ii) The molecular system under study as well as the reference systems can be in different electronic states I and J , respectively.

As a consequence of this multidimensional variation each kind of reference system has its own distance matrix with the elements $d(I,J)$, $I=0,1,2,\dots$, $J=0,1,2,\dots$ [28]. The elements of the distance matrix are well defined but not all of them impart useful physical insights. Therefore, application is restricted to only a few of them. In spite of that their variety is large enough to open a broad field of applications. In this chapter three main directions to apply distance measures will be considered.

One important direction is the analysis of electronic states which allows a deeper understanding of u.v. spectral data (section 3.1).

State analysis may also be the starting point for new classification schemes. This is particularly useful in the case of excited states whose properties and electronic structures are not too well known.

State analysis can comprise state correlation between iso-electronic systems (section 3.1.1) or state description in terms of weakly interacting sub-units. The best fit composite model, as defined in section 2.3.4.1, cannot be unambiguously derived from chemical intuition or experience. Attempts along this line are frequently misleading for the ground state of molecules and well-nigh impossible for excited states. In this respect, partial distance measures are well-suited to substantiate theoretically certain breakdown schemes. For ground state molecules this is done in section 3.1.2. The partial distance measures offer different classifications of excited states: (i) The excitation can be localized in a certain molecular sub-unit whereas the rest of the molecule is quasi-nonexcited (locally excited states, section 3.1.3); (ii) Considerable charge transfer from one sub-unit to the other can occur upon excitation. (This is mostly connected with a dramatic change of polarity and the formation of two weakly coupled open shell structures, section 3.1.4).

Sometimes it is of interest to investigate electronic transitions. In section 3.2 the applicability of distance measures to their characterisation will be discussed.

Distance measures are able to reveal loosely coupled molecular sub-units, excited or nonexcited, with even or odd electrons; one has to expect that certain physicochemical properties of molecules which depend on the electronic structure are also interpretable by means of distance measures (section 3.3).

In section 3.3.1 and 3.3.2 distance measures are employed to study the effects of different solvents on conjugated systems and the controversial concept of aromaticity, respectively. Partial distance measures are found to be useful indices for the Diels-Alder reactivity of alternant hydrocarbons (section 3.3.3). Finally, the analysis of excited states is connected with the course of photoreactions (section 3.3.4) and with the propagation of excitation energy from a local region to the whole molecular system as a consequence of geometrical relaxation in excited states (section 3.3.5).

3.1 STATE ANALYSIS

3.1.1 STATE CORRELATION

State correlation diagrams have been established as instructive tools to comparatively interpret u.v. spectra of related compounds. A further application concerns the relations between the electronic states of initial and final products of chemical reactions. In this way correlation diagrams provide basic knowledge about whether a certain reaction path is allowed or forbidden [5].

Conventionally, there are two prerequisites for deriving practicable correlation diagrams. First, the relative energies of the states and their sequence must be known as correctly as possible.

Secondly, correlating states must belong to the same irreducible representation. The latter condition restricts conventional correlation diagrams to systems having at least one symmetry element more than the symmetry plane. In the case of molecules belonging to the C_S point group arbitrary states within the σ - or the π -manifold correlate to each other. Since initial and final products of chemical reactions as well as their transients are frequently of low symmetry, information about state correlation would be instructive and desirable by means of methods which are not assisted by symmetry. Examples of attempts to avoid these problems are the use of local symmetry elements of reactions centres [5] and the extension of the symmetry-assisted Hoffmann-Woodward rules to unsymmetrical cases [38].

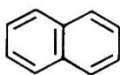
The projection of iso- π -electronic states in the framework of Configuration analysis [16] is also a reasonable alternative. This method works for states of arbitrary symmetry since the symmetry of the wavefunctions is fully involved in the mathematical procedure. This kind of correlation seems to be even superior to the bare assignment based on symmetry: through the projection technique each detail of the wavefunction is scanned and compared with the corresponding detail of the reference wavefunction. Configuration analysis permits therefore quantitative correlation of states independent of the molecular symmetry.

In this connection the question arises to what extent distance measures can act as indicators for state correlation. It could be imagined that state crossings might cause sudden changes of the electronic structure and, therefore, they becomes recognizable by large values of the distance measures.

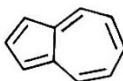
However, this expectation is seriously restricted: Derived from the square of the wavefunction, the P-matrix reflects only the molecular symmetry but not the symmetry of the state wavefunctions. This makes the method "blind" for discriminating states of similar electronic structure but different symmetry. Consequently for each pair of states, independent of their symmetry, small distances and therefore "some correlation" will be obtained. As a striking example for this deficiency may serve the excited $\pi\pi^*$ states of benzene which have identical P-matrices although they belong to different symmetry classes.

In spite of this drawback it seems to be worthwhile to investigate the useability of distance measures as indicators of state correlation.

As an example naphthalene (1) and azulene (2) are compared with 10-annulene (3) which can be considered as the common parent molecule for 1 and 2; considered are the three electronic states S_0 , S_1 , and S_2 .



1



2



3

The distance measures, collected in the following table, reflect the change in the electronic structure of 3 due to the intraannular bond (forming 1 and 2).

		<u>1</u>			<u>2</u>		
<u>3</u>	J \ I	0	1	2	0	1	2
	0	152	115	136	74	148	96
	1	155	99	124	83	139	82
	2	155	100	124	83	139	82

In Fig. 1 the distance measures $d(I,J)$ (where $I = J$) are connected with the state energies and the projection values obtained from configuration analysis (values in brackets [24]).

From the figure the following conclusions can be drawn:

- (i) Introduction of an intraannular bond into the 10 π -perimeter molecule strongly influences the electronic structure of naphthalene in the states S_0 and S_2 and of azulene in the state S_1 , as evidenced by the high $d(I,J)$ values. The correlation of these states with those of the parent compound 3 is therefore considered as weak. The state S_1 in 1 and S_0 and S_2 in 2 are much less affected by this change. They are more strongly correlated with the corresponding states of the reference system 3.
- (ii) Large distance measures correspond to low projection indices of configuration analysis [24] and vice versa. These relations are generally fulfilled in Fig. 1.

3.1.1 MOLECULAR SUB-UNITS OF MOLECULES IN GROUND AND EXCITED STATES

The individuality of the sub-units T and U (see section 2.3.4.1) incorporated in the composite molecular system $M = T-U$ can be investigated by means of the partial distance measures

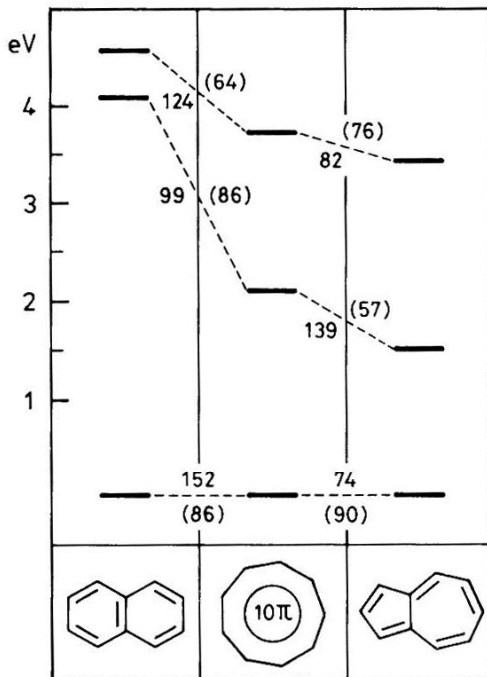
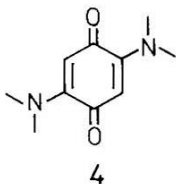


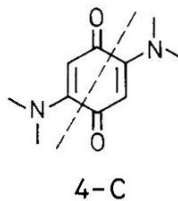
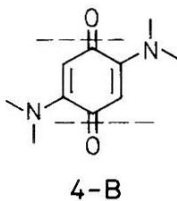
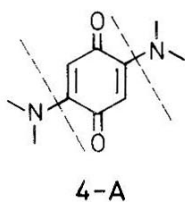
Fig. 1. State correlation of 1 and 2 with 3. The values in brackets have been obtained from configuration analysis [24].

between the P-submatrices of T or U and the P-matrices of the isolated reference systems T_0 and U_0 . Both the molecule under study and the reference molecules are assumed to be in the ground state. Following chapter 2 the specific partial distance measures are denoted by $d_T(0,0)$ and $d_U(0,0)$.

In the first example, 2,5-diamino-quinone (4)



will be fragmented mentally into three alternative groups of sub-systems. Decomposition mode 4-A considers 4 as quinone (T) with two amino groups, whereas in fragmentation pattern 4-B the main subunit is p-phenylene-diamine (T). Mode 4-C finally separates the molecule into two trimethine-merocyanine sub-units as originally proposed in [39].



$d_T(0,0)$ 84

220

25

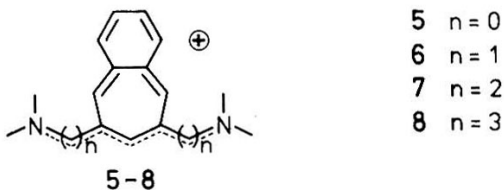
The distance measures favour clearly 4-C as the best fit description confirming Dähne's proposal [39]. A strong argument supporting 4-C is the extremely large bond length between the carbonyl and the amino substituted carbons that has been determined to be 1.54 Å by X-ray spectroscopy [8]. The two other decomposition modes are less favoured, at least in the ground state

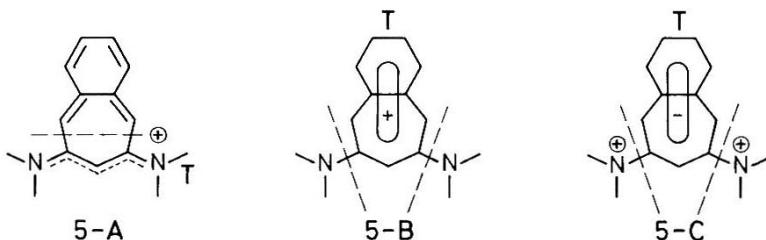
(see below), but not out of discussion.

Particularly 4-A could be a useful fragmentation if properties of quinones should be investigated comparatively. However, distance measures reveal and predict that the quinone character is only weakly manifested in 4.

In this sense we want to underline two important aspects. First, the best fit description is the most reasonable classification of a molecule in terms of sub-units; but it is not necessarily the unique one. Second, the different electronic states may correspond to different best fit descriptions, e.g. the S_1 -state of 4 is best described as 4-A (see Table 1 of Appendix).

The next examples deal with three alternative modes of decomposition for a set of homologue molecules. In this case distance measures are expected to vary characteristically depending on two factors: the decomposition modes and the length of the polymethine chains.





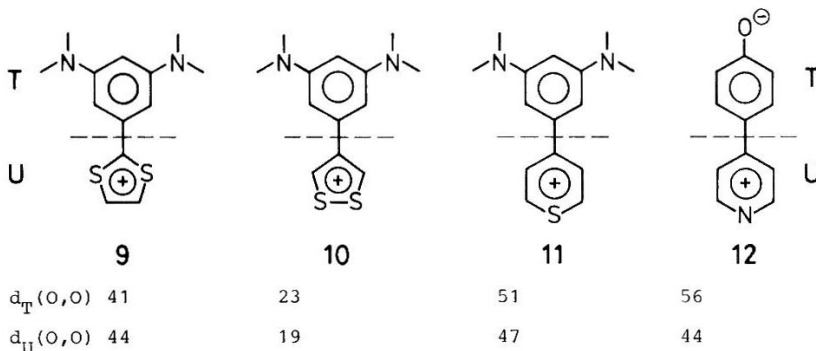
$d_T(0,0)$

<u>5</u>	114	<u>87</u>	<u>204</u>
<u>6</u>	<u>27</u>	174	287
<u>7</u>	94	<u>62</u>	207
<u>8</u>	<u>26</u>	157	275

The distance measures under the formulae show clearly that decomposition schemes 5-B and 7-B are the best ones for 5 and 7, respectively, classifying these compounds as di-substituted tropyllium cations. In contrast to that, 6 and 8 "prefer" the decomposition mode A, i.e. these molecules should be considered as a penta-, respectively nona-methine cyanine cation symmetrically bridged by an o-benzoquinodimethane sub-unit. Modes 5-C to 8-C composing the molecules from the antiaromatic tropyllium anion are evidently without any importance for the description of these compounds. These examples show that the best fit decomposition mode can vary even in the case of very closely corresponding molecules [29]. The alternation between two different fragmentation modes may be correlated with the number of π -electrons in the fragments. Coupling of subunits to form a total of $4N$ π -electrons ($4m + 2/4r + 2$ or $4m/4r$) indicates mode A,

whereas combinations of subunits to form a total of $4N + 2 \pi$ -electrons ($4m + 2/4r$ or vice versa) result in substituted quasi-aromatic rings [29].

The last example presents the molecules 9 - 12 decomposed into separate rings.



In all these examples strong donors are coupled with strong acceptors. Normally in such cases a comprehensive electron re-organization upon coupling should be expected in order to smooth the large gradients in spatial electron density. The low distance values, however, give evidence that charge equalization does not occur noticeably in the ground state.

The best fit description in terms of molecular subunits for 37 organic π -molecules in ground (S_0) and excited states ($S_1, S_2, S_3, S_4, S_5, T_1$) is given in Table 1 of the Appendix.

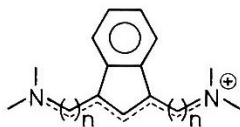
3.1.3 LOCALLY EXCITED STATES

Locally excited states are those in which the excitation energy is localized in a certain spatial region, say T,

of a molecule T-U, and no strong interaction between the subunits, T^{••} and U, takes place.

Hence, locally excited states are indicated by small values for both distance measures, $d_T(I,J)$ and $d_U(I,O)$. The sub-units T and U need not be the same as those for the best fit decomposition of the ground state. On the contrary, very often new sub-units are to be defined in order to comprehend the phenomenon of local excitation. Attention should be paid to the fact that the term "locally excited state" holds primarily for the state of vertical excitation. It can be shown that for most π -conjugated systems the localization of excitation energy is preserved after geometrical relaxation to the energetic minimum (spectroscopic minimum) of the corresponding excited state.

In the first example alternative decomposition modes for the S_1 state are tested for the compounds 13 - 16.



13-16

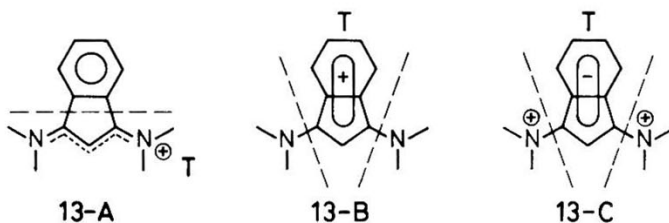
13: n=0

14: n=1

15: n=2

16: n=3

Similar to compounds 5 - 8 in section 3.1.2 three alternative ways of mental decomposition are studied:

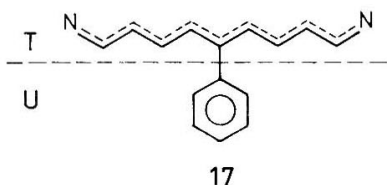


	$d_T(1,1)$		
<u>13</u>	109	<u>61</u>	187
<u>14</u>	<u>50</u>	141	175
<u>15</u>	<u>75</u>	89	180
<u>16</u>	<u>22</u>	139	150

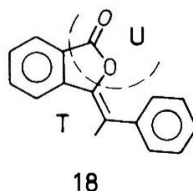
The comparison of distance measures shows that decomposition mode C can be omitted from further consideration. 13 in the S_1 -state can be considered as 1,3-diamino-substituted S_1 -excited benzo-cyclopentadienylium cation (mode B). Compounds 14 and 16 can be satisfactorily interpreted as locally excited polymethine chains (mode A); however, the coupling of the subunits polymethinecyanine cation and benzene is considerably higher than in the ground state. The last indicates electron reorganization upon excitation: as seen from the unnormalized values for compounds 13-16, mode A, in [29], systematically $d_T(1,1) > d_T(0,0)$, and $d_U(1,0) > d_U(0,0)$. For compound 15, decomposition modes A and B are approximately equally applicable. This demonstrates the limit of fragmentation models. Obviously, this excited state can

be better described as delocalized over the whole system.

Of course, also higher excited states can have local excited character as can be seen for the molecules 17 - 19. The modes of decomposition are indicated by dotted lines.

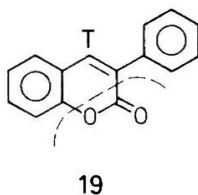


$$d_T(2,1) = 30$$



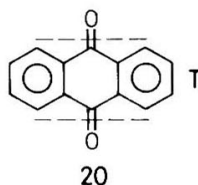
$$d_T(2,2) = 34$$

$$d_T(3,3) = 27$$



$$d_T(2,2) = 47$$

$$d_T(3,3) = 46$$



$$d_T(5,J) > 105$$

$$\text{for } J = 1, 2, 3, 4, 5$$

The partial distance measures support some empirical assignments of u.v. bands. Thus, in the UV/VIS spectra of benzilidenphthalide 18 and phenylcoumarine 19, the second absorption band is very similar to that in the spectrum of the stilbene chromophore; for 18 and its CN-derivative in para position in the phenyl ring, the observed spectral similarity is illustrated on Fig. 2.

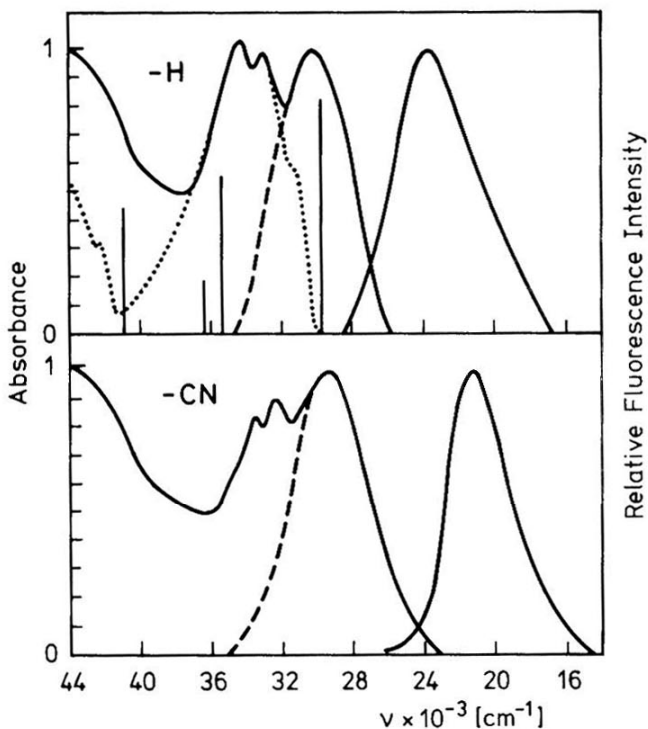


Fig. 2. Spectra of benzylidene phthalide and its CN-derivative in para position in the phenyl ring. First absorption band after deconvolution ... spectrum of stilbene.

d_T for the 5-th excited state of anthraquinone 20 show that this state cannot be interpreted as locally excited.

Further examples for local excitation in the first and higher excited electron states are presented in Table 1 of the Appendix.

3.1.4. INTRAMOLECULAR CHARGE TRANSFER UPON EXCITATION

As we have seen electronic transitions are accompanied by the reorganization of charges and bond orders of the molecular system being excited. In the last sub-section this reorganization localized to one sub-system whereas the other one remained more or less in its electronic ground state.

Furthermore it can occur that excitation exerts strong transfer of electron density from one sub-unit to the other. This case is particularly probable for molecules consisting of weakly coupled sub-units which have strong donor and acceptor character, respectively. The formal result of a complete intramolecular charge transfer upon excitation is then a pair of radicals. If we assume that T is the donor and U the acceptor sub-unit of the molecule T-U the result of the excitation can be described as follows:



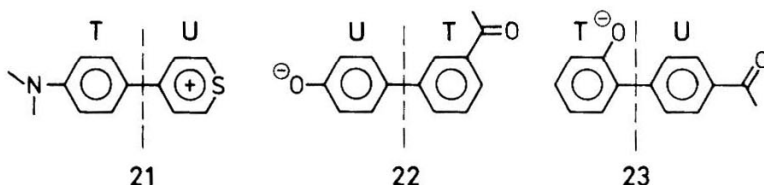
However, the charge transfer remains very often incomplete in contrast to redox processes in ions or to intermolecular complex or exciplex formation of organic molecules accompanied by intermolecular electron transfer [40].

Electronic states of this kind have been frequently characterized by summation of the charge transferred. However, this is only a rough measure to describe the transfer process because it gives no information about the resulting distribution of this charge.

In order to characterize intramolecular charge transfer states in terms of distance measures we start with the idea that the

two sub-units should resemble the electronic structure of the radicals T_O^+ and U_O^- which offer themselves as proper references molecules. Small partial distance measures $d_T(I,J)$ and $d_U(I,J)$ are therefore proposed as indicators for a strong intramolecular charge transfer.

In order to illustrate the interpretative possibilities of $d_T(I,J)$ and $d_U(I,J)$ the molecular systems 9-12 (see subsect. 3.1.2) and 21-23 will be considered with respect to their excited singlet states S_1 , S_2 and S_3 . The results are collected in the following Table.



In the ground state each of the systems can be interpreted as consisting of two weakly coupled closed shell sub-units although strong donors are linked with strong acceptor parts. (This has been shown explicitly for 9-12 in subsection 3.1.2). In the S_1 -state the situation is completely changed. Now the closed shell distance measures $d_T(1,1)$ and $d_U(1,1)$ are very large indicating a strong perturbation of the electronic structure upon excitation. On the other hand, with the exception of 22, the open shell distance measures $d_T(1,0)$ and $d_U(1,0)$ are rather low. This proves that excitation generates in good approximation a corre-

Partial distance measures for 9-12 and 21-23 based on closed and open shell reference systems. In the last column, subscripts 0,1 indicate states S_0, S_1 of reference subunits.

Com- pound	I	J	Closed shell reference donor T	acceptor U	open shell reference donor T	acceptor U	Notation of state
<u>9</u>	1	0	123	226	<u>34</u>	<u>46</u>	$T_0^* - U_0^*$
	1	1	98	229	114	270	

	2	0	160	208	149	<u>49</u>	$T_1^* - U_0^*$
	2	1	153	227	<u>84</u>	265	

<u>10</u>	3	0	91	224	129	258	
	3	1	108	172	133	111	

	1	0	136	216	<u>35</u>	<u>61</u>	$T_0^* - U_0^*$
	1	1	124	192	129	191	

<u>11</u>	2	0	153	214	139	<u>59</u>	$D_1 - D_0$
	2	1	159	190	<u>64</u>	190	$T_1^* - U_0^*$

	3	0	110	131	<u>64</u>	178	
	3	1	68	197	124	127	

<u>12</u>	1	0	133	177	<u>31</u>	<u>51</u>	$T_0^* - U_0^*$
	1	1	114	171	121	204	

	2	0	155	170	136	<u>50</u>	$T_1^* - U_0^*$
	2	1	150	167	<u>65</u>	200	

<u>12</u>	3	0	148	184	<u>48</u>	185	$T_0^* - U_1^*$
	3	1	126	234	130	<u>84</u>	

	1	0	145	152	<u>63</u>	<u>61</u>	$T_0^* - U_0^*$
	1	1	268	143	191	216	

<u>12</u>	2	0	153	169	<u>68</u>	190	$T_0^* - U_1^*$
	2	1	258	196	187	<u>54</u>	

	3	0	123	114	149	<u>81</u>	$T_1^* - U_0^*$
	3	1	237	133	<u>84</u>	192	

Table (contnd.)

<u>21</u>	1	0	140	152	<u>93</u>	<u>65</u>	$T_0^* - U_0^*$	
	1	1	148	152	192	197		

	2	0	132	137	161	<u>74</u>	$T_1^* - U_0^*$	
	1	1	180	161	<u>71</u>	189		

3	0	145	159	108	176			
3	1	166	203	189	92			
3	2	162	191	105	157			

<u>22</u>	1	0	130	66	103	114		
	1	1	260	109	173	157		

	2	0	<u>45</u>	117	158	129	$T_0 - U_1$	
	2	1	253	<u>77</u>	137	173		

3	0	<u>55</u>	115	159	127	$T_0 - U_1$		
3	1	251	<u>96</u>	131	173			

<u>23</u>	1	0	134	90	<u>87</u>	<u>99</u>	$T_0^* - U_0^*$	
	1	1	268	104	172	163		

	2	0	<u>52</u>	96	125	141	$T_0 - U_1$	
	2	1	253	<u>63</u>	140	111		

3	0	<u>89</u>	<u>62</u>	139	111	$T_0 - U_1$		
3	1	235	89	125	158			

lated radical pair weakly coupled. It is interesting to see that in the S_1 -states the ground state electronic structures of the radicals are implemented.

The S_2 -state of the compounds 9-12 and 21 are overwhelmingly characterized by charge transfer into the same direction. The amount of charge being transferred is similar as in S_1 and allows no differentiation of the two states. However, the partial distance measures reveal that the electronic structure of the donor (9-11, 21) or of the acceptor (12) part resembles closely that of the first excited state radical. Thus, the S_2 -state of these compounds can be described as a locally excited radical pair. The S_3 -state of 11 and 12 are also locally excited radical pairs, but the excitation is now localized in the opposite part.

In the same way as S_2 and S_3 some higher excited singlet states, S_n , might have its best fit description as locally excited radical pairs, $T'_O(JT) - U'_O(JU)$, as well; this exhibits some parallelism to experimental results [41] obtained in the intermolecular case of some complexes.

The formation of pronounced radical pairs upon excitation is due to a weak coupling between the sub-units. Stronger coupling is indicated by a larger value of the distance measure for the open shell reference system. Such excited states have no typical CT character; the amount of transferred electronic density upon excitation is small. This tendency is demonstrated by the compounds 21-23. S_1 and S_2 of 21 as well as S_1 of 23 exhibit some CT character whereas S_2 and S_3 of 22 and 23 can rather be interpreted as locally excited states of the closed shell sub-units.

Further examples for intramolecular CT states are presented in Table 1 of the Appendix.

3.2 ANALYSIS of ELECTRON TRANSITIONS

3.2.1. ANALYSIS OF THE ELECTRON EXCITATION USING A REFERENCE SYSTEM L=M(O)

The distance approach can be also applied for the analysis of electron transitions.

Let us consider a vertical (Franck-Condon) transition from the ground(O) to a given excited state (I) of the molecule M=T-U. The electron excitation of the molecule T-U is characterized by the change in the electron density distribution, which is represented by the matrix $\Delta P(I)$

$$\Delta P(I) = P(I) - P(O) \quad (3.2.1)$$

where $P(O)$ and $P(I)$ are the Coulson charge-bond order matrices in ground and excited states, respectively.

$$\Delta P(I) = \left[\begin{array}{c|c} \Delta P_T(I) & \\ \hline & \Delta P_U(I) \end{array} \right] \quad (3.2.2)$$

$\Delta P_T(I)$ and $\Delta P_U(I)$ reflect the change in the electron density distribution in the subunits T and U, respectively. The squares of the partial distances

$$d_T^2[P_T(I), P_T(O)] = \sum_{\mu, \nu \in T} [P_{\mu\nu}^T(I) - P_{\mu\nu}^T(O)]^2 = \sum_{\mu, \nu \in T} [\Delta P_{\mu\nu}^T(I)]^2 \quad (3.2.3)$$

$$d_U^2[P_U(I), P_U(O)] = \sum_{\mu, \nu \in U} [P_{\mu\nu}^U(I) - P_{\mu\nu}^U(O)]^2 = \sum_{\mu, \nu \in U} [\Delta P_{\mu\nu}^U(I)]^2$$

may be considered as an unequivocal criterion for estimating the localisation of the electron excitation within the fragments T or U. It is convenient to relativate d_T^2 and d_U^2 with the square of the total distance

$$d^2[P(I), P(O)] = \sum_{\substack{\mu, \nu \in T \\ \in U}} [P_{\mu\nu}(I) - P_{\mu\nu}(O)]^2 = \sum_{\substack{\mu, \nu \in T \\ \in U}} [\Delta P_{\mu\nu}(I)]^2 \quad (3.2.4)$$

where $\bar{d}_T = d_T^2/d^2$, $\bar{d}_U = d_U^2/d^2$, and $\bar{d}_T + \bar{d}_U = 1$. If the whole electron excitation is confined to the molecular subunit T, then $\bar{d}_T = 1$, and $\bar{d}_U = 0$. If however $\bar{d}_T \approx \bar{d}_U$, it is obvious that the electron excitation is more or less delocalised over the whole molecule T-U or an exciton-like excitation is present. It is easy to find out which of the two possibilities is realised by studying the bond order of the bond connecting T and U in the studied state I: if the bond is weak ($P < 0.3$) we have exciton-like excitation, if it is strong ($P \geq 0.5$) we have delocalised electron excitation.

Formulae (3.2.2)-(3.2.4) can easily be generalized for an arbitrary number of molecular subunits.

In the above treatment, if we do not use the Euclidean (d_2) distance measure, but the absolute distance measure (d_1), formulae (3.2.3)-(3.2.4) become identical to the criteria for the localisation of the electron excitation introduced in an empirical way by Sukhorukov and coworkers [42].

Examples which illustrate the above approach, are given in Table 2 of the Appendix.

3.2.2 ANALYSIS OF THE ELECTRON EXCITATION USING A REFERENCE SYSTEM $L = \{T_0, U_0\}$

In the preceding paragraph the matrix $\Delta P(I)$ was defined, reflecting the change in the electron density distribution upon excitation of the molecule $M=T-U$ from the ground to a given excited state I . Let us juxtapose the molecule $T-U$ and a reference system T_0, U_0 consisting of two uncoupled subunits T_0 and U_0 . The excitation $O-J$ in the reference system will cause a change in the electron density distribution in the reference subunits T_0 and U_0 , and this will be represented by the matrix $\Delta P_0(J)$

$$\Delta P_0(J) = P_0(J) - P_0(O) \quad (3.2.5)$$

where $P_0(O)$ and $P_0(J)$ are block diagonal matrices consisting of the charge-bond matrices of the ground and excited state of the reference units: $P_{T_0}(O)$; $P_{U_0}(O)$, $P_{T_0}(JT)$, $P_{U_0}(JU)$. JT and JU need not be equal.

$$\Delta P_0(J) = \begin{bmatrix} \Delta P_{T_0}(JT) & 0 \\ 0 & \Delta P_{U_0}(JU) \end{bmatrix} \quad (3.2.6)$$

$\Delta P_{T_0}(JT)$ and $\Delta P_{U_0}(JU)$ represent the change in the electron density distribution in the reference subunits T_0 and U_0 , correspondingly.

The specific partial distances

$$d_T[\Delta P_T(I), \Delta P_{T_O}(JT)] = \left\{ \frac{1}{n_T} \sum_{\mu, \nu \in T} [\Delta P_{\mu\nu}^T(I) - \Delta P_{\mu\nu}^T(JT)]^2 \right\}^{1/2} \quad (3.2.7)$$

$$d_U[\Delta P_U(I), \Delta P_{U_O}(JU)] = \left\{ \frac{1}{n_U} \sum_{\mu, \nu \in U} [\Delta P_{\mu\nu}^U(I) - \Delta P_{\mu\nu}^U(JU)]^2 \right\}^{1/2}$$

are a measure of the similarity between the change in the electron density distribution in T and T_O (resp. U and U_O) upon excitation of the molecule T-U and of the reference system T_O, U_O. n_T and n_U are the number of P_{μν} elements in the subunits T and U.

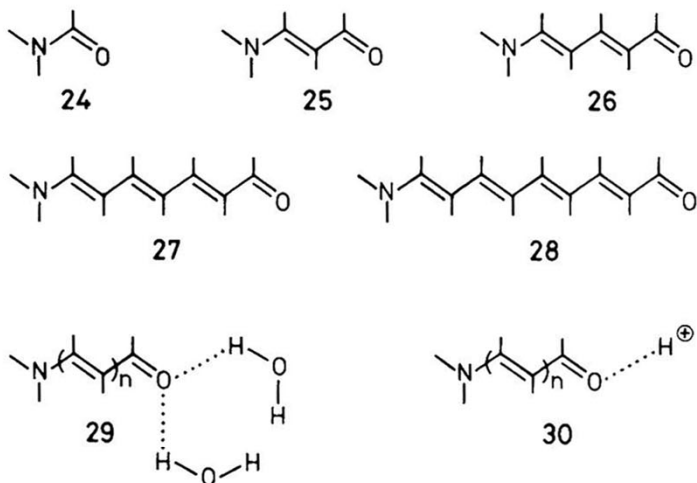
If the excitation is confined predominantly to the subunit T, a low value for d_T, and a high value for d_U will result, and vice versa.

We shall illustrate this approach on several examples collected in Table 3 of the Appendix.

3.3 DISTANCE MEASURES AND PHYSICO-CHEMICAL PROPERTIES OF MOLECULES

3.3.1 INTERMOLECULAR FORCES - SOLVENT EFFECTS

Two interacting molecules M₁ and M₂ change their electronic structure when approaching each other. Besides the energetic stabilization or destabilization of the supermolecule M₁...M₂ relative to the molecules at infinite distance, the induced electronic reorganization in both sub-units expressed by distance measures could be used as a criterion to evaluate the strength of the interaction. Energetic stabilization and electronic reorganization need, however, not be parallel. The latter must



rather be considered as complementary information about the intermolecular interaction.

A good example of intermolecular interactions extensively studied in quantum chemistry is the solute-solvent interaction. The distance measure between the solute molecule M surrounded by solvent molecules, S, and the isolated "gaseous" molecule M is proposed as a measure of its electronic modification.

We shall use for illustration the vinylogue unbranched chains of ω -aminopolyeneals (merocyanines) 24-28 which are known to exhibit a sensitive response to different solvent environments. This could be established by the solvent shift of the n.m.r. signals in ^1H and ^{13}C -spectra [43,44] as well as by considerable

positive solvatochromism of the long wavelength u.v. absorption band [45-47]. The latter suggests that the S_1 -state is more stabilized by protic solvents than the ground state.

The compounds 24-28 were treated quantum chemically using the INDO/S method [48]. Two molecules of the solvent-water and one proton as the simplest model for protonic acids were arranged around the carbonyl group as shown in 29 and 30, respectively. The supermolecules of the dihydrated and protonated merocyanines 24-28 were then calculated in the same manner. The geometry of the dihydrates was adapted to data from the literature [49].

The position of the proton resulted from geometry optimization for the protonated small chains 24 and 25 plus proton [47]. Geometrical relaxations of the solute due to the solvent molecules have been neglected.

In the following the influence of the solvents on the π -systems of 24-28 in the electronic states S_0 and S_1 will be discussed. The total distance measures $d(0,0)$ and $d(1,1)$ resulting from comparison of the dihydrated and protonated chains with the corresponding isolated systems 25-28 are graphically presented, as a function of the chain length in Fig. 3.

The values lead to the following conclusions:

- (i) In the ground state the total distances of the dihydrated and protonated chains slightly increase with increasing chain lengths.
- (ii) Due to the higher polarization power the proton affects the electronic structure of the chains much stronger than water; in accordance to that $d(I,I)$, $I=0,1$, are about one order smaller for dihydrated than for protonated systems.

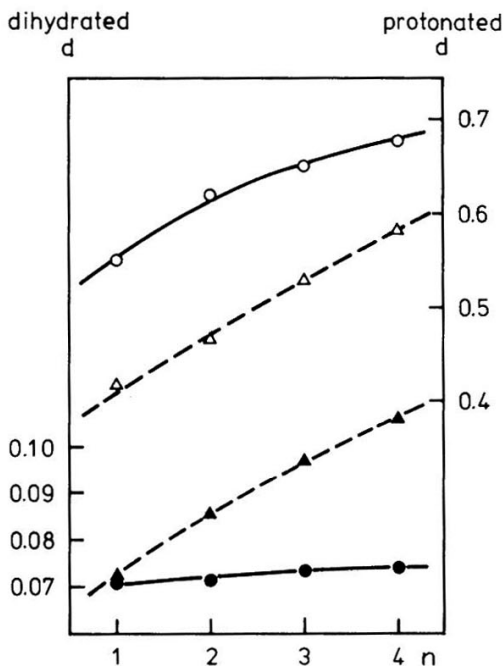
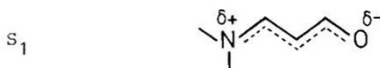


Fig. 3. Total distance measures (non-specific) of dehydrated and protonated merocyanine chains as a function of the chain length. $\circ - S_0(H_2O)$. $\circ - S_0(H^+)$. $\Delta - S_1(H_2O)$. $\Delta - S_1(H^+)$.

- (iii) The dihydrates deviate in the first excited singlet state more strongly than in their ground states from the corresponding electronic structure of the unsolvated chains.
- (iv) The influence of the proton on the excited π -systems 25-28 is smaller than in the ground state.

If we specify the distances in relation to the number of elements in the P-matrix, eq. (2.13), the averaged influence of the solvent on the chain decreases with increasing chain length, i.e. the specific distance measure behaves contrary to the non-specific one shown in Fig. 3. This behaviour agrees with the truism that small molecules are much more affected by solvents than larger ones and it also explains conclusion (i).

A calculation of the electronic structure of merocyanines and the respective supermolecules of type 29 and 30 [47] has shown that the ground states of the merocyanines are characterized by strong bond alternation and small charge transfer from N to O, whereas the first excited states have nearly equal bond orders but a strong charge alternation [50].



Hence, the protonation affects the electronic structures of the ground states more strongly than those of the excited states which explains why $d(1,1) < d(0,0)$ for protonated systems (Fig. 3).

From an energetic point of view water as well as the proton causes stabilization of the $\pi\pi^*$ -excited states of merocyanine chains. This stabilization is for protons much higher than for two water molecules. Furthermore, in both cases the S_1 state is more strongly stabilized than the ground state [47]. The better stabilization of the S_1 states could, perhaps, explain why $d(1,1) > d(0,0)$ for dihydrated merocyanines.

3.3.2 OVERALL AND LOCAL AROMATICITY [27]

Aromaticity is still a matter of interest for chemists although its definition is far from being transparent [51]. Aromaticity is connected with a certain additional stability of cyclic conjugated compounds and their inclination to essentially retain their conjugated system in the course of a chemical reaction. Different kinds of resonance energies have been accepted as important indicators for the additional energetic stabilization of these compounds [52-54]. Recently possibilities for other approaches to the discussion of aromaticity have been offered [55].

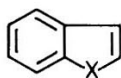
On the other hand also other physical properties are brought into connection with the term aromaticity. Thus the diamagnetic ring current which influences the chemical shifts of ring protons in n.m.r. spectroscopy or magneto-optical properties which prove cyclic conjugated compounds to be in an exceptional position have been proposed for proper criteria of aromaticity [56].

From a more theoretical point of view two different approaches can be distinguished for the definition of aromaticity. First, additional energy stabilization is required relative to certain reference structures which are non-aromatic in the sense of the definition. The choice of the reference system is one of the weakest points of these approaches. The resonance energies are positive and indicate stabilization especially for cyclic conjugated compounds with $4n + 2$ π -electrons obeying Hückel's rule. The opposite is true for anti-Hückel compounds having $4n$ π -electrons in the cycle. Second, some properties which are unam-

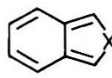
bigously derived from the wavefunction are assumed to be inherent for aromatic compounds. Besides their magnetic properties, aromatic compounds are characterized by particular features of their electronic structure: The π -electrons are distributed uniformly over the atoms of the ring and the CC bond distances are observed to have equal lengths. Therefore, the idea suggests itself to compare the wave function or derived values therefrom of a certain molecular system with the corresponding cyclic conjugated perimeter defined as being aromatic. In other words, the distance measure $d(O,O)$ between a cyclic conjugated compound and the iso- π -electronic carbocyclic reference system (which obeys the Hückel rule) may be used as criterion for the similarity of the two electronic structures and therefore as a new index of aromaticity.

If we consider bicyclic conjugated systems with different heteroatoms the reference system can be chosen twofold. In a first approach the system can be compared with the iso- π -electronic perimeter molecule neglecting all intra-annular bonds. In this case the bond lengths equalization and charge delocalization along the molecular periphery is studied. The total distance $d(O,O)$ becomes the criterion of overall aromaticity. On the other hand local criteria of aromaticity can also be defined by using partial distance measures $d_T(O,O)$ which reflect the implementation of a local aromatic structure (e.g. benzene) within the polycyclic compound.

As an example the indices of overall and local aromaticity are calculated for the heterocyclic compounds which are of the "benzenoid" (31 to 33) and of the "quinoid" (34 to 36) type.



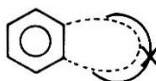
31-33



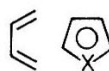
34-36



37 (model A)



38 (model B)



39 (model C)

The reference system for the overall aromaticity is the perimeter [9] annuleny-anion 37 (model A) whereas the local aromaticity is described by the analysis of 31-36 with respect to the benzene-heteroene 38 (model B) or butadiene-heterocycle 39 (model C).

As in other fields of applications distance measures can be calculated also for excited states. Thus, deviations from the ideal aromatic electronic structure upon excitation can be obtained as well.

In the Table below the overall distance measures for the compounds 31-36 with reference to model A are collected for the electronic states S_0 , S_1 and S_2 . Additionally, the partial distances reflecting local aromaticity criteria following models B and C and the resonance energies obtained from energy differences to the corresponding open-chained compounds (in which X is terminal) are given for comparison [54].

Specific distance measures for compounds 31-36, following models A - C

Compound	Overall aromaticity (model A)			Reson. Energy ^{a)} β-units	Local aromaticity	
	d(0,0)	d(1,0)	d(2,0)		Model B d _T (0,0) ^{b)}	Model C d _U (0,0) ^{c)}
<u>31</u>	171	170	154	0.047	75	71
<u>32</u>	199	174	163	0.044	56	77
<u>33</u>	210	210	213	0.036	57	75

<u>34</u>	162	171	150	0.029	139	52
<u>35</u>	190	194	162	0.025	156	49
<u>36</u>	205	209	189	0.002	155	46

a) Taken from Ref. [54]

b) partial distance to benzene (T)

c) partial distance to the heterocycle (U)

The results can be summarized as follows:

- (i) Low distance measures mean close correspondence to the carbocyclic reference systems and therefore high overall or local aromaticity. Within both the benzenoid and the quinoid structural types the overall aromaticity index for the ground state, d(0,0), decreases in the sequence N > S > O. For each separate class of compounds this is in agreement with the order of resonance energies.
- (ii) The electronic structure of the quinoid compounds 34-36 is found to be very slightly more similar to that of the perimeter than that of benzenoid heterocycles 31-33. In

this sense 34-36 are "more aromatic" than compounds 31-33. This contradicts the values of resonance energies which provide the opposite result. This suggests that analysis of the electronic structure evidently reveals different aspects of the complex property "aromaticity" than the analysis of the energetics.

This absence of congruence between different criteria of aromaticity has its striking equivalent in the consideration of experimental results. Whereas for alternant hydrocarbons the energetic stability increases with the diamagnetic ring current, experimental studies suggest that this is not true for non-alternant hydrocarbons and heterobenzenes [57-59].

(iii) The electronic structure of the compounds is not considerably changed upon excitation. Therefore, the distance measures $d(1,0)$ and $d(2,0)$ are not much different from those of the ground state. Also the sequence among the different types of compounds is preserved for these states. In summary, compounds 31-36 retain their aromatic electron structures in the first two low-lying excited states although they become destabilized energetically due to the excitation.

(iv) The partial distance measures obtained from the decomposition schemes B (38) and C (39) show a consistent picture: For compounds 31-33 the aromatic benzenoid sub-unit dominates whereas in the series 34-36 the five-membered heterocycle is well implemented.

The small values obtained for partial distances demonstrate that local aromatic electron structures are much better

implemented than the characteristics of the perimeter molecule.

The dominance of the heterocyclic delocalization (model C, 39) for the quinoid heterocycles accounts for the fact that heteroatoms exert a negligible effect on the residual butadienic sub-units. This can be supported by n.m.r. studies which provide the ratio of the two coupling constants within the butadien sub-unit as nearly constant and independent of the heteroatom [60].

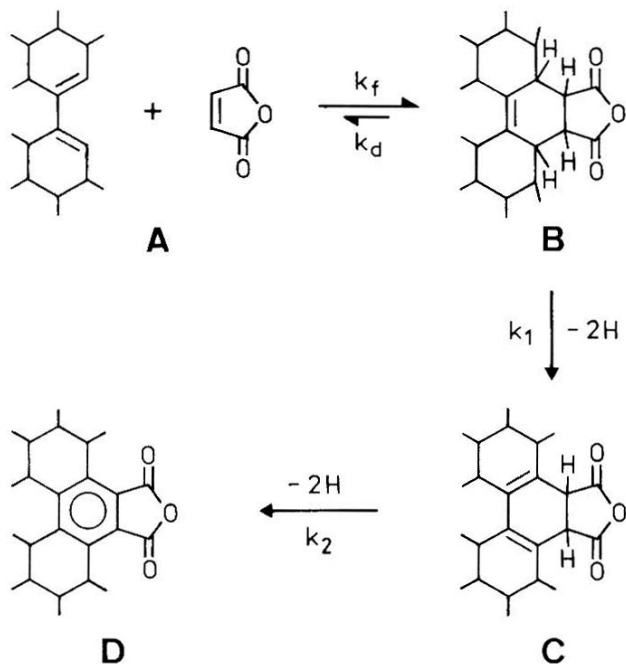
Distance (similarity) measure was used [83] to characterize two groups of diazaaromatics: "normal" and "anomolous." It was shown that proton addition and electronic excitation lead to much larger distance values in "anomolous" quinoxaline (= 1,4-diazanaphthaline) than in "normal" phthalazine (= 2,3-diazanaphthaline).

3.3.3. THERMAL REACTIVITY

Most of chemical reactions may be typified with respect to the arrangement of the centers where they take place and the mechanism they follow; examples of that are the Claisen condensation, Beckmann rearrangement, etc. In a series of reactions of one and the same type the relative reactivity of the individual systems should be reflected by the distance measures which express quantitatively the amount of chemical analogy. In other words, the distance measures should be related to the rate (equilibrium) constants in the case of kinetic (thermodynamic) control of the reaction. But when the distance measures are defined by means of P-matrices, as done in Sect. 2,

they represent global differences in the electronic structures of the individual reaction systems; thus a close correlation with the rate rather than with the equilibrium constants has to be expected since the latter ones depend more on changes of energy than on changes of the electronic structure. In accordance with this, till now, no thermodynamically controlled reaction has been found which may be discussed in terms of distance measures.

As an example for a kinetically controlled reaction the benzogenic Diels Alder reaction [61] may serve. This reaction consists of the addition of maleic anhydride (MA) onto a periph-
eric cisoid C_4 -unit of a polycyclic aromatic hydrocarbon (PAH) in the presence of a dehydrogenating reagent and follows the mechanism below:



The primarily formed adduct B, is most probably generated in an one step addition. It is in equilibrium with the starting material, A. The equilibrium usually favours A, but it is perturbed by the dehydrogenation reaction via C to D. The intermediate C has been traced in some special cases [62]. The overall reaction, i.e. the formation of D, takes place if $k_1 > k_d$.

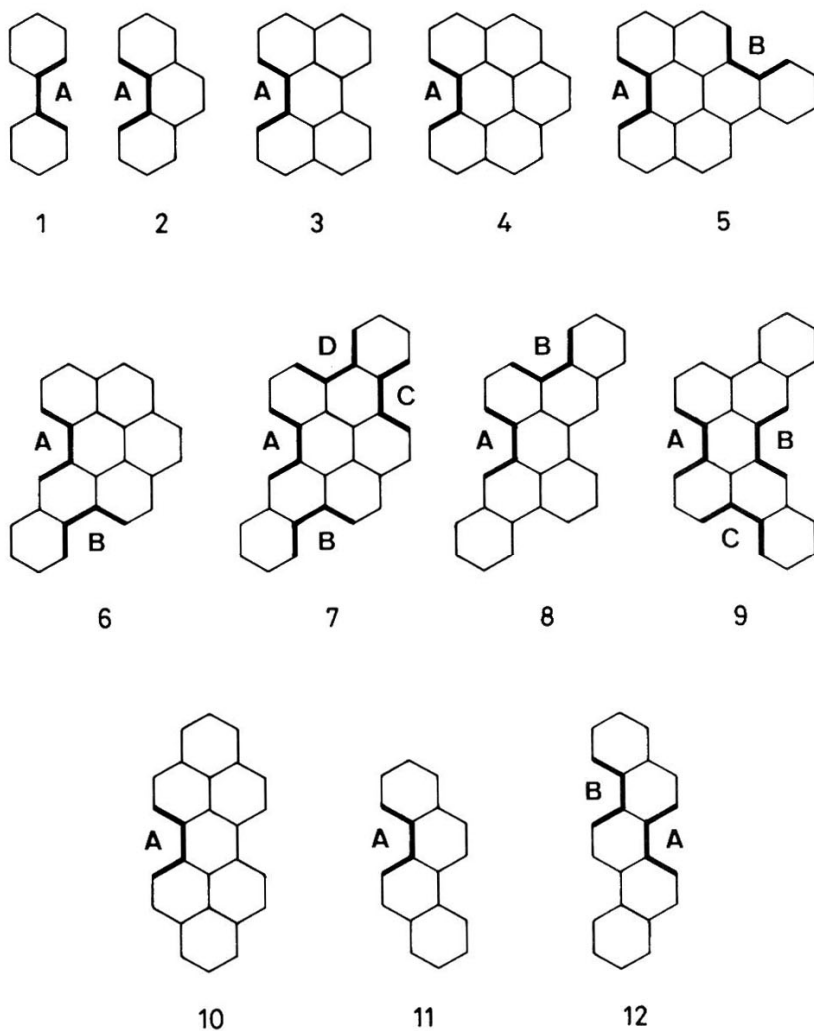


Fig. 4. Some polycyclic aromatic hydrocarbons and their peripheric cisoid C_4 units, where the benzogenic Diels-Alder-reaction could take place

Since k_1 and k_2 only depend on the redox potential of the dehydrogenating agent used (nitrobenzene or chloranile) and k_d is nearly independent from the structure of A, the overall rate of the formation of D is proportional to k_f . This means that the overall reaction is controlled by the kinetics of the primary addition and, hence, it should be suited for a discussion in terms of distance measures with reference to the ground state of butadiene.

In Fig. 4 some selected PAH's are shown; their inequivalent peripheric cisoid C_4 -units are marked by A, B, C and D. In the following Table the specific partial distance measures (derived from HMO data of these C_4 -units with reference to the ground state of butadiene) are collected.

Firstly from several different C_4 -units of amolecule (as in 5-9 and 12) just that one should react most rapidly which exhibits the highest analogy to butadiene indicated by the smallest d-value. Since with a single exception [62] all PAH's add only one molecule of MA if at all, it should be possible to derive the structure of the product formed from the relative magnitude of the d-values. Inspection of the Table shows that this expectation is realized.

Secondly, the Table shows that the addition takes place if $d \leq 14,51 \cdot 10^{-3}$, but no reaction has been observed if $d \geq 15,02 \cdot 10^{-3}$. This points to a critical value of the distance measure, d_{crit} , for this reaction which is in the range of $14,5 < 10^3 d_{crit} < 15,0$.

A critical value in a kinetically controlled reaction must be understood as the indication of an upper limit for the quanta

Nr. of Comp.	Mol. Subunit	$d \cdot 10^3$	Relative Rate Constant [63]	MA- addition [61]
1	A	15.02		-
2	A	16.29		-
3	A	13.46	220	+
4	A	14.51	1	+
5	A	14.01	7	+
	B	17.42		
6	A	13.03	38	+
	B	17.60		
7	A	13.36	9	+
	B	22.03		
	C	16.65		
	D	15.59		
8	A	12.68	175	+
	B	16.18		
9	A	14.07		
	B	11.08		+
	C	16.17		
10	A	19.40		-
11	A	17.93		-
12	A	19.44		
	B	17.39		-

of activation heat available under the conditions of the reaction. But such an interpretation of d_{crit} implies, that the logarithms of the rate constant of formation, k_f , correlate with d in general. This is supported by Fig. 5 which shows a fairly good correlation of the statistically corrected relative rate constants [63] with the d -values. From this a linear free energy relationship may be derived, namely

$$\Delta G^\ddagger = a + b \cdot d$$

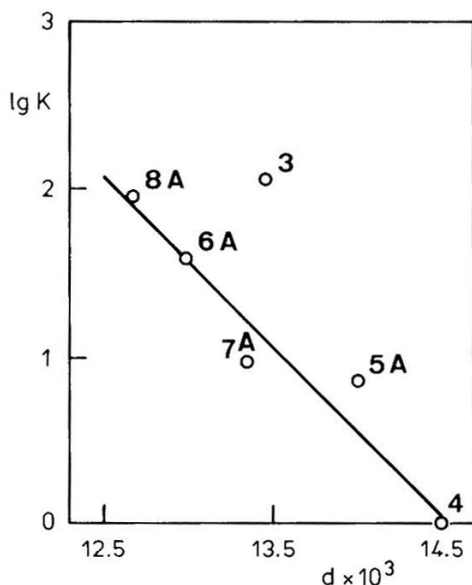


Fig. 5. Correlation of the logarithm of the reaction rate constants under standard conditions [63] with the partial distance measure, $d \cdot 10^3$, of the reacting C units

where ΔG^\ddagger is the free enthalpy of activation for the addition and a and b are suitable constants, whose meaning is illustrated by Fig. 6 [64]. Assuming that the geometries of the reaction centers of the activated complexes formed from MA and either any PAH or butadiene do not differ significantly then all these activated complexes should have nearly the same content of free enthalpy, i.e. all the reaction profiles obtained for these additions should coincide in their respective maxima. Then, a corresponds to the free enthalpy of activation in the addition of MA to butadiene. $b \cdot d$, on the other hand, indicates an additional demand on energy mainly necessary for the polarisation of

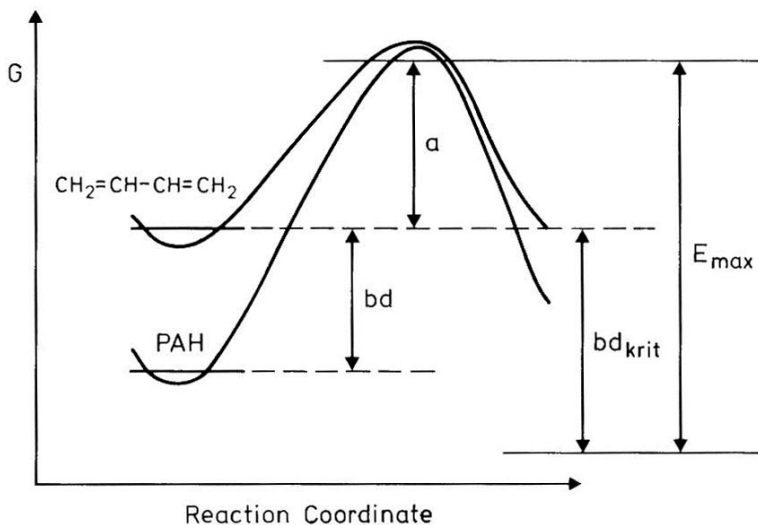


Fig. 6. Schematic reaction profiles for the MA addition to butadiene and a polycyclic aromatic hydrocarbon (PAH). Under certain experimental conditions a maximal energy of activation, E_{\max} , is available on which the critical value of d depends

the actual electronic structure in the reacting C_4 -unit of the PAH to make it butadiene-like.

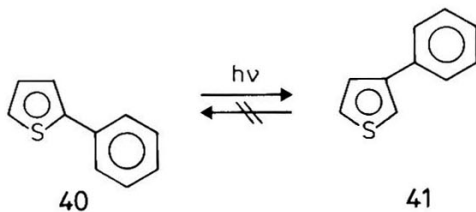
Since the benzogenic Diels-Alder-reaction is carried out under the same thermal conditions (boiling nitrobenzene) there is an upper limit, E_{\max} , for the energy quanta available for activation; obviously, d_{crit} is related to E_{\max} , namely

$$b \cdot d_{\text{crit}} = E_{\max} - a.$$

3.3.4 PHOTOREACTIVITY

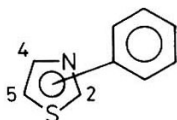
In many cases photochemical reactions have their origin in the lowest excited singlet state. The course of the reaction is well reflected by the potential surfaces of both the S_1 and the S_0 state of the reacting system [65,66]. However, potential surfaces are accessible only in a very approximative way. Fortunately there is evidence for a great number of photo-reactions that the initial properties of the S_1 state conduct the photochemical reaction into a certain reactive channel and become responsible for a specific reaction course. This means that the initial character of the excited state might reveal information about its potential photoreactivity. As has been demonstrated in section 3.1, total and partial distance measures are proper tools for the analysis of excited states. This section describes their useability as indices of photoreactivity.

It is well established from extensive investigations that 2-phenyl-thiophene undergoes rearrangement into 3-phenyl-thiophene under irradiation [67,68]. Careful studies show the reaction to be irreversible. No traces of 2-phenyl-thiophene have been detected after irradiation of pure 3-phenyl-thiophene. However, the latter compound suffers a very complex rearrangement within the five-membered ring leading accidentally



always back to 3-phenyl-thiophene [69] ("no reaction" reaction).

Similar photochemical properties are found for phenyl-thiazoles and phenyl-isothiazoles 42-47 [70,71].

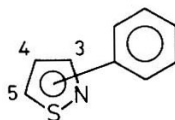


42-44

2-Ph: **42**

4-Ph: **43**

5-Ph: **44**



45-47

3-Ph: **45**

4-Ph: **46**

5-Ph: **47**

Here the final products of the photochemical rearrangement of all the isomers are 43 and 46 together with small amounts of 45, and they are photochemically stable.

The different photochemical behaviour of molecules with similar structure suggests the formation of photointermediates of different geometry during the reaction. This gives rise to the question if different intermediates result also from different excited states [69].

In the Table below the states S_1 and S_2 of all mentioned compounds are characterized by the partial distance measures $d_T(1,1)$, $d_T(2,2)$ and $d_U(1,0)$, $d_U(2,0)$ (T-phenyl subunit, U-heterocyclic subunit).

compound	$d_T(1,1)$	$d_U(1,0)$	$d_T(2,2)$	$d_U(2,0)$
<u>40</u>	112	159	47	66
<u>41</u>	36	50	112	146
<u>42</u>	106	173	32	60
<u>43</u>	36	17	112	138
<u>44</u>	106	161	47	67
<u>45</u>	51	57	96	144
<u>46</u>	29	46	101	164
<u>47</u>	106	151	39	57

The following classification may be derived:

- (i) For compounds 40, 42, 44, 47 the distance values $d_T(1,1)$ and $d_U(1,0)$ are large indicating no local similarity of the phenyl sub-unit to the electronic structure of excited benzene. The S_1 states of these compounds can therefore be interpreted as delocalized. The transitions leading to these states have high oscillator strengths. All compounds of this group undergo isomerization by irradiation.
- (ii) Compounds 41, 43, 45 and 46 are characterized by very low distance measures $d_T(1,1)$ connected with a low value for $d_U(1,0)$. The S_1 -state of these compounds can therefore be considered as locally excited in the phenyl sub-unit. The oscillator strength of the corresponding transition is low and suggests that the S_1 -state corresponds closely to the L_b -state in benzene weakly perturbed by the heterocyclic ring. Obviously, this state prefers another channel of photochemical rearrangement; these compounds undergo the "no-

reaction" reaction, they are "photochemically stable".

Comparing the values of $d_T(1,1)$ and $d_T(2,2)$ for all compounds studied it is evident that the two different kinds of excited states are interchanged. The locally excited state is S_1 in 41, 43, 45 and 46 but S_2 in 40, 42, 44 and 47.

Finally it should be emphasized that this application of distance measures has only classifying but not predicting character, as the nature of an electronic state permits no firm conclusion to be made concerning its photoreactive behaviour. However, analysis of excited states by distance measures can promote understanding of the alternative reactive channels of limited groups of compounds.

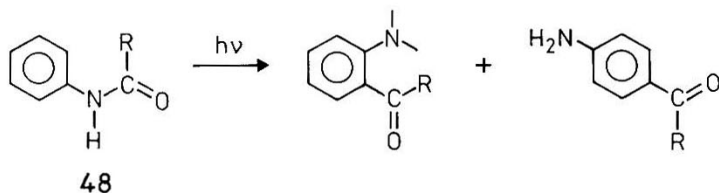
3.3.5 INDICATION OF ENERGY TRANSFER

The mutual influence of two approaching molecules on their electronic structure has been already subject of section 3.3.1 (solute-solvents interactions). This mutual effect is expected to be even stronger in the case of chemical reactions. Section 3.3.3 described static relations between distance measures and the inclination for specific thermal reactions considering only the initial systems. However the potential along certain reaction pathways is accompanied by the successive change of the electronic structure of both reactive components. Less is known so far if there exist also critical geometrical regions where the electronic structure of the supermolecule suffers decisive changes indicating the completion of the chemical reaction and if so, what relations hold between these geometrical situations and the extrema of the potential surface.

Recently Bader et al. investigated the dissociation of H_2O into H_2 (1^1g^+) and O (1^1D) with respect to the change of the electronic structure along the C_{2v} -symmetrical reaction pathway [72]. As a result of ab initio calculations the gradient vector field of the electron density functions becomes accessible and provides contour diagrams. For increasing O-H distances a so-called catastrophe point suddenly occurs indicating the homolytic decay of the O-H bond and the formation of the H-H bond. It can be expected that distance measures based on the comparison of the sub-units in the supermolecule with the initial and final molecular systems will provide similar results.

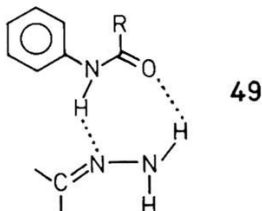
At present only preliminary calculations of distance measures for some specific points of the potential curves of a photochemical reaction are available.

It is well known that N-aryl-urethanes and -anilides undergo photo-Fries-reaction under irradiation [73-75].



This reaction is found to be inhibited by aliphatic hydrazones. This quenching process cannot be caused by energy transfer since aliphatic hydrazones can not act as energy acceptors in such a process. But the hydrazones might be able to form molecular encounter complexes (49) with the urethane or the arylamide

via H-bonds, which in turn allow energy dissipation by proton transfer within the H-bridges [76-78].



In Fig. 7 the potential curves obtained by CNDO/2 [79] for S_0 and EHP [80] for S_1 and S_2 , are shown for the complex 49; the lengths of the two H-bridges $NH\dots O$ and $NH\dots N$ distances are assumed equal [81,82].

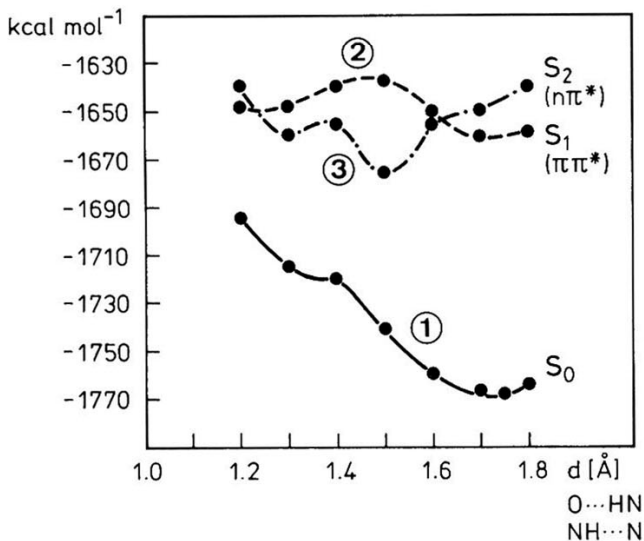


Fig. 7. Potential curves of the simultaneous displacement of the hydrogens towards the proton acceptor atoms in the states S_0 , S_1 and S_2 . The numbers in the minima label the cases discussed in the text

It can be seen that in the ground state there is one main minimum between 1.7 and 1.8 Å, and this is the expected distance in the H-bridges. A second minimum much higher in energy appears at a shorter distance.

In the $\pi\pi^*$ excited state (S_1) the energies of these two minima are very similar indicating the potential possibility of proton transfer. Minimum 2 is the spectroscopic minimum [65] of the complex primarily achieved upon excitation. If the protons are shifted for about 0.2 Å, a third state shows strong energy depression and even "forbidden" crossing with the potential curve of the $\pi\pi^*$ state occurs. This state originates in the $n\pi^*$ state of 48 and is modified by a strong admixture of an intermolecular charge transfer state. The non-spectroscopic minimum 3 of this state is lower in energy than minimum 2 and could act as a trap for the system's radiationless deactivation preventing the arylamide from undergoing the photo-Fries rearrangement. Of course, the potential curves have been obtained in a very approximative way and the results can be considered only as a qualitative general model for the generation of competitive deactivation channels of excited molecules.

In the following Table the partial distance measures for N-phenylformamid (T) and for formaldehyd-hydrazone (U) in the molecular complex 49, for the minima 1-3, are collected:

minimum	I	J	$d_T(I,J)$	$d_U(I,J)$
1	0	0	23	14
2	1	1	23	396
	1	0	96	0
3 ^{a)}	1	1	218	366
	1	0	185	324

a) For minimum 3, data for S_1 are given (I=1), because of the crossing of the curves for S_1 and S_2 .

These data are interpreted as follows:

minimum 1: The ground state minimum of 49 shows only weak interaction of the two molecules. Their electronic structure is only little affected by each other. This corresponds to our experience for the solvent water which also influenced the molecules 24-28 via H-bridges.

minimum 2: In the spectroscopic minimum the partial distances $d_T(1,1)$ and $d_U(1,0)$ have very low values. In line with section 3.1.3, the $S_1 \pi\pi^*$ -state is locally excited in the arylamide sub-unit whereas the hydrazone has practically retained its ground state electronic structure. This means that the total excitation energy is concentrated in the arylamide.

minimum 3: On increasing the length of the H-bridges by 0.2 \AA , a dramatic change of the electronic structure occurs. In the non-spectroscopic minimum 3 the decomposition of the supermolecule into the original sub-structures is no longer justified. Both sub-systems show considerable changes of their electronic structure due to a sudden polarization through energy transfer from hydrazone to the arylamide. The excitation energy must be assumed henceforth as delocalized over the whole complex. The hydrazone moiety is now fully involved in the excitation, the load of the arylamide with respect to the excitation energy has been diminished.

Distance measures become in this case indicators for the delocalization of excitation energy within the supermolecule.

4. EVALUATION AND CONCLUSIONS

The Euclidean distance measures as defined in Section 2. allow a new kind of secondary data processing of quantum chemical results. Distance measures can be understood as indices which reflect chemical analogy and other essential features of the electronic structure of molecules in any electronic states of interest. They are easily derivable from the charge-bond order matrices.

The basic idea of distance measures consists in comparing two electronic structures and in determining quantitatively the degree of their similarity. They reflect the specific deviation of two electronic states with respect to their electronic structure. The motivation of such comparisons is the assumption that states with similar electronic structures show also similar physical and chemical properties if these are mainly determined by the electronic structure.

Distance measures are of the same importance as character orders and projection indices from configuration analysis. The simple definition allows distance measures to be easily obtained and widely applied. The range of application involves charge-bond order matrices which can be derived from ab initio as well as semiempirical quantum chemical methods. Ground state and excited electronic states of molecules with odd or even numbers of electrons can be treated equally well.

The type of comparison may be very different. The i th electronic state of a molecule can be compared with the J th state of the same molecule, with the J th state of an iso-electronic re-

ference system or with different sets of uncoupled reference molecules which correspond to molecular sub-units of the molecule under study. Each set can be obtained by a mental breakdown of the system investigated.

The main applicative field for distance measures is the characterization of electronic states with respect to their electronic structure. The degree of similarity to a definite reference state allows the classification of electronic states. The classification for conceptual purposes is based on the revelation of characteristic sub-units which can be considered as weakly interacting building blocks in the ground state of molecules, on the localization of excitation energy in a definite molecular part, on characteristic electronic reorganizations upon excitation via intramolecular electron transfer within different molecular sub-units, and the electronic relatedness of different electronic states in iso-electronic and/or iso-topological systems.

Comparison of two different electronic states of the same molecule provides information about changes in the electronic structure upon excitation, thus aiding to understand the character of electronic transitions.

The peculiarities of electronic states reflected by their charge-bond order matrices partially govern their physico-chemical properties. In this context distance measures become theoretical correlation parameters to specific molecular properties. The examples given deal with the effects of different solvents on solute molecules, with the aromatic character of molecules in different electronic states, with thermal and photochemical

reactivity of molecules as a consequence of specific state characteristics and with the redistribution of excitation energy along a specific photochemical reaction coordinate.

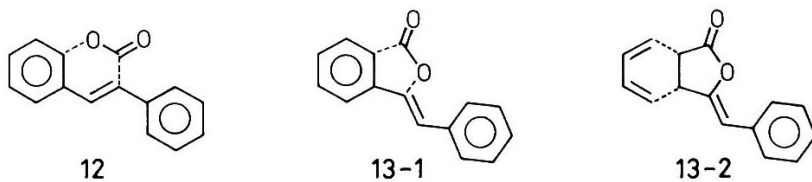
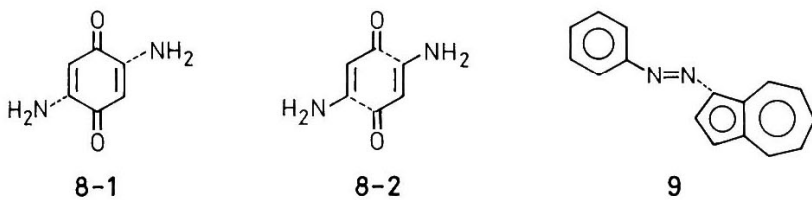
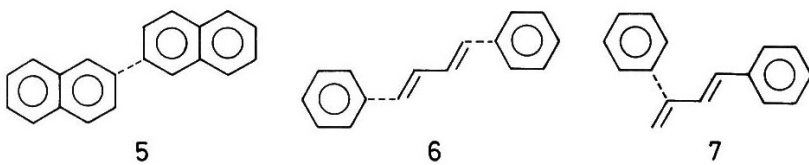
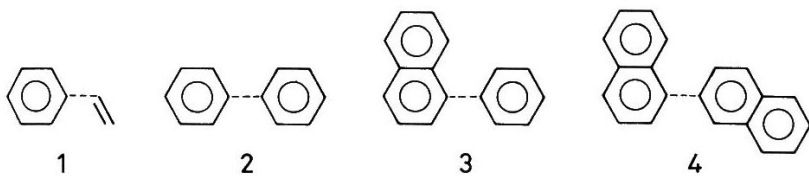
Distance measures allow transparent physical interpretation only if they are small. In our scale this is normally fulfilled for values of $d < 100$. Large distance measures bear no more information than that the states compared are dissimilar.

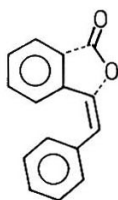
Distance measures surpass other methods of state analysis by their versatility. However, they disregard the state symmetry and can be only restrictively applied for state correlation.

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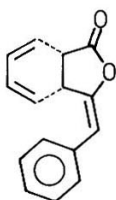
6. APPENDIX

Here some additional examples to subsections 3.1.2, 3.1.3, 3.1.4, and Section 3.2. are presented: the best fit description in terms of molecular submits of some selected organic π -molecules (Table 1), the analysis of some electron transitions using a reference system $L=M(O)$ (Table 2) and $L=(T_O U_O)$ (Table 3), respectively. The structures investigated and their respective decomposition are given in the following formula scheme.

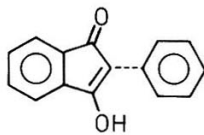




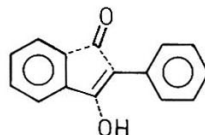
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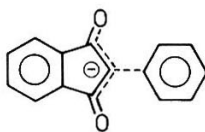
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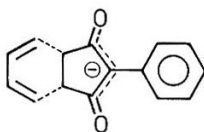
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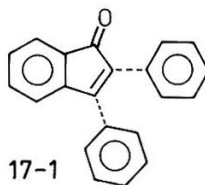
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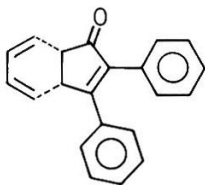
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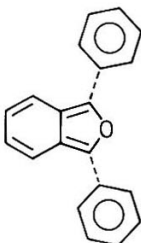
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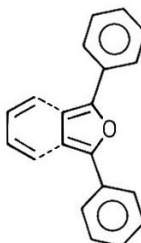
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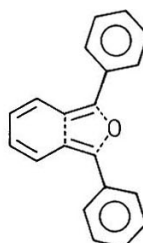
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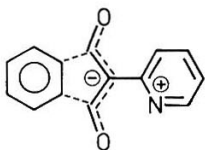
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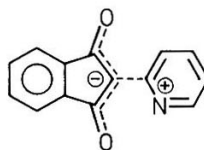
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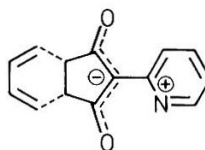
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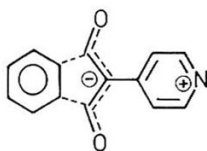
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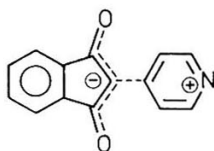
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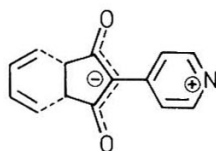
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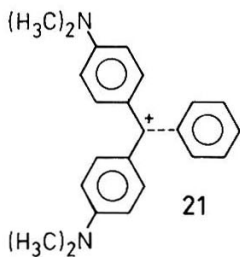
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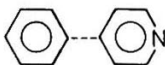
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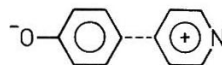
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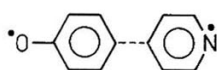
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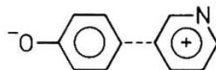
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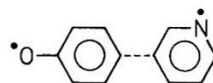
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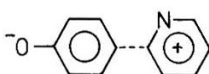
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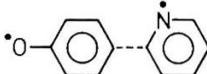
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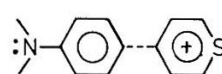
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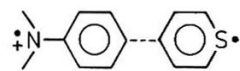
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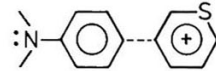
25-2



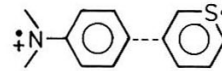
26-1



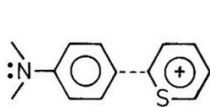
26-2



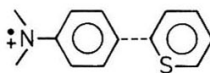
27-1



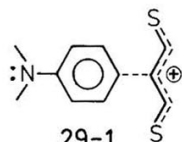
27-2



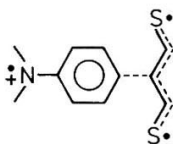
28-1



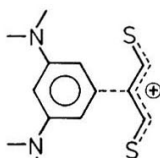
28-2



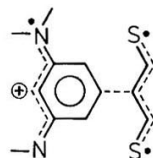
29-1



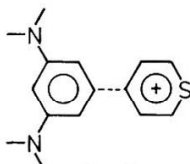
29-2



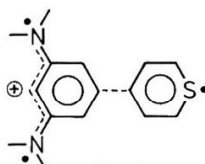
30-1



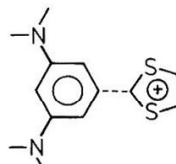
30-2



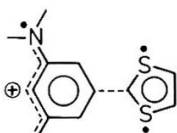
31-1



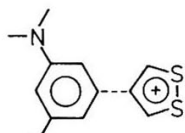
31-2



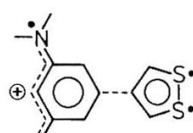
32-1



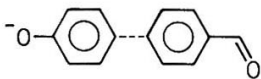
32-2



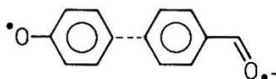
33-1



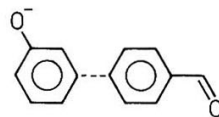
33-2



34-1



34-2



35-1

Table 1. State analysis. Singlet states (S_0, S_1, \dots) are denoted by their subscripts (0,1,...).

Nr. of comp.	State I	Best fit reference system	States of ref.units		Partial distances for subunits		Total distance
			left	right	left	right	
1	0	1	0	0	10	37	23
	1	1	1	0	104	272	163
	2	1	1	0	10	77	38
	3	1	1	0	55	143	86
	4	1	1	0	140	49	134
2	5	1	1	0	87	283	153
	0	1	0	0	5	5	5
	1	1	1	1	57	57	57
	2	1	1	1	57	57	57
	3	1	1	1	106	106	106
3	4	1	1	1	57	57	57
	0	1	0	0	3	4	3
	1	1	1	0	3	5	4
	2	1	0	0	17	21	19
	3	1	0	1	10	10	10
4	4	1	2	0	56	87	69
	5	1	2	0	43	77	58
	0	1	0	0	3	3	3
	1	1	0	1	0	8	9
	2	1	1	0	4	5	5
5	3	1	2	0	33	40	37
	4	1	0	2	24	23	24
	5	1	2	2	50	55	53
	0	1	0	0	5	5	5
	1	1	1	1	34	34	34
5	2	1	1	1	33	33	33
	3	1	0	0	52	52	52
	4	1	2	2	48	48	48
	5	1	0	0	44	44	44

Table 1. State analysis. Singlet states (S_0, S_1, \dots) are denoted by their subscripts (0,1,...).

Nr. of comp.	State I	Best fit reference system	States of ref.units left	States of ref.units right	Partial distances for subunits left	Partial distances for subunits right	Total distance	
6	0	1	0	0x2	32	15x2	20	
	1	1	T_1	0x2	72	55x2	59	
	2	1	0	1x2	60	60x2	60	
	3	1	0	1x2	60	60x2	60	
	4	1	0	0x2	123	58x2	78	
	5	1	0	0x2	109	79x2	87	
7	0	1	0	0	12	9	10	
	1	1	0	1	22	17	19	
	2	1	0	2	12	9	10	
	3	1	1	0	16	23	21	
	4	1	1	4	111	66	86	
8	0	2	0	0	25	25	25	
	1	1	1	0x2	56	254x2	100	
	2	1	2	0x2	60	269x2	106	
	3	1	3	0x2	64	229x2	97	
	4	2	0	0	126	126	126	
9	0	1	0	0	28	21	24	
	1	1	0	1	22	18	20	
	2	1	0	2	89	69	78	
	3	1	0	4	74	41	58	
	4	1	0	3	76	50	63	
10	0	1	0	0	5	5	5	
	1	1	1	0	10	11	11	
	2	1	0	1	14	11	13	
	3	1	2	0	76	78	77	
	4	1	0	2	54	73	63	
11	0	1	0	0	6	17	13	
	1	1	1	0	9	18	15	
	2	1	0	1	14	25	21	
	3	1	0	0	105	95	100	
	4	1	0	0	68	64	66	

Table 1. State analysis. Singlet states (S_0, S_1, \dots) are denoted by their subscripts (0,1,...).

Nr. of comp.	State I	Best fit reference system	States of ref.units		Partial distances for subunits		Total distance
			left	right	left	right	
12	0	1	0	0	33	62	39
	1	1	1	0	47	79	53
	2	1	2	0	47	74	52
	3	1	3	0	46	61	48
13	0	1	0	0	27	40	29
	1	1	1	0	50	82	56
	2	1	2	0	34	63	40
	3	1	3	0	27	44	30
14	0	1	0	0	27	38	29
	1	1	1	0	62	82	65
	2	1	2	0	46	66	44
	T_1	1	T_1	0	55	149	84
15	0	1	0	0	6	22	14
	1	1	1	0	22	30	25
	2	1	2	0	10	22	15
	T_1	1	T_1	0	7	22	14
16	0	1	0	0	45	55	49
	1	1	1	0	44	54	48
	2	1	2	0	48	66	55
	T_1	1	T_1	0	51	51	51
17	0	1	0	0x2	9	6,14	10
	1	1	1	0x2	31	16,29	27
	2	1	2	0x2	12	7,14	12
	T_1	1	T_1	0x2	13	11,21	15
18	0	1	0	0x2	15	17x2	16
	1	1	1	0x2	58	44x2	51
	2	1	2	0x2	80	29x2	57
	T_1	1	T_1	0x2	21	25x2	23
19	0	1	0	0	52	23	44
	1	1	1	0	112	65	95
	2	1	2	0	127	38	102
	T_1	1	T_1	0	24	57	48

Table 1. State analysis. Singlet states (S_0, S_1, \dots) are denoted by their subscripts (0,1,...).

Nr. of comp.	State I	Best fit reference system	States of ref.units		Partial distances for subunits		Total distance	
			left	right	left	right		
20	0	1	0	0	51	20	42	
	1	1	1	0	43	22	37	
	2	1	2	0	134	91	121	
	T_1	1	T_1	0	42	21	36	
21	0	1	0	0	16	36	23	
	1	1	1	0	11	27	17	
	2	1	4	0	46	107	69	
	3	1	4	1	67	163	103	
	4	1	2	0	11	28	17	
	5	1	2	0	12	27	18	
22	0	1	0	0	5	5	5	
	1	1	1	0	9	14	12	
	2	1	0	1	15	10	13	
	3	1	1	3	118	82	102	
	4	1	0	0	62	68	65	
23	0	1	0	0	56	44	51	
	1	2	0	0	63	61	62	
	2	2	0	1	68	54	62	
	3	2	1	0	94	71	83	
24	0	1	0	0	47	33	41	
	1	2	0	0	61	39	52	
	2	2	0	1	66	69	67	
	3	1	3	0	100	68	87	
25	0	1	0	0	58	43	52	
	1	2	0	0	65	88	76	
	2	2	0	1	64	91	78	
	3	1	3	0	97	80	90	
26	0	1	0	0	82	74	78	
	1	2	0	0	93	65	81	
	2	2	1	0	71	74	72	
	3	2	2	1	105	92	99	

Table 1. State analysis. Singlet states (S_0, S_1, \dots) are denoted by their subscripts (0,1,...).

Nr. of comp.	State I	Best fit reference system	States of ref.units		Partial distances for subunits		Total distance	
			left	right	left	right		
27	0	1	0	0	47	29	40	
	1	2	0	0	84	36	66	
	2	2	0	1	88	90	89	
	3	2	1	0	26	47	37	
28	0	1	0	0	77	76	77	
	1	2	0	0	95	80	88	
	2	2	3	1	94	156	126	
29	3	2	0	1	99	90	95	
	0	1	0	0	35	19	30	
	1	2	0	0	80	75	78	
30	2	1	0	1	47	31	41	
	3	2	1	0	60	74	66	
	0	1	0	0	26	16	23	
	1	2	0	0	29	73	50	
31	2	2	1	0	70	73	71	
	3	1	0	1	63	89	73	
	0	1	0	0	51	47	49	
	1	2	0	0	31	51	41	
32	2	2	1	0	65	50	59	
	3	2	0	1	48	84	66	
	0	1	0	0	41	44	42	
	1	2	0	0	34	46	39	
33	2	2	1	0	84	49	73	
	3	2	2	0	76	111	91	
	0	1	0	0	23	19	22	
33	1	2	0	0	35	61	47	
	2	2	1	0	64	59	62	
	3	2	0	1	64	127	93	

Table 1. State analysis. Singlet states (S_0, S_1, \dots) are denoted by their subscripts (0,1,...).

Nr. of comp.	State I	Best fit reference system	States of ref.units		Partial distances for subunits		Total distance
			left	right	left	right	
34	0	1	0	0	15	16	16
	1	2	0	0	107	91	99
	2	1	0	0	125	24	87
	3	1	0	1	32	32	32
35	0	1	0	0	12	15	14
	1	1	0	0	130	66	101
	2	1	0	1	45	77	64
36	3	1	0	1	55	96	80
	0	1	0	0	19	18	18
	1	2	0	0	87	99	94
	2	1	0	1	52	63	58
37	3	1	0	0	89	62	76
	0	1	0	0	58	25	38
	1	1	1	1	134	92	107
	2	1	1	2	183	101	132
	3	1	0	1	69	28	45

Table 2. Analysis of Electron Transitions according to eqs. 3.2.3 and 3.2.4

Nr. of Compound	Transition O→I	\bar{d} left	\bar{d} right
<u>1</u>	1	0.5126	0.4874
	2	0.9668	0.0332
	3	0.8250	0.1750
<u>2</u>	1	0.5000	0.5000
	2	0.5000	0.5000
	3	0.5000	0.5000
	4	0.5000	0.5000
<u>3</u>	1	0.9995	0.0005
	2	0.9790	0.0210
	3	0.0069	0.9931
	4	0.4462	0.5538
	5	0.5811	0.4189
<u>4</u>	1	0.0087	0.9913
	2	0.9991	0.0009
	3	0.7821	0.2179
	4	0.0839	0.9161
	5	0.4616	0.5384
<u>7</u>	1	0.9964	0.0560
	2	1.0000	0.0000
	3	0.0317	0.9683
	4	0.4576	0.5424
<u>10</u>	1	0.9969	0.0031
	2	0.0074	0.9926
	3	0.6845	0.3155
	4	0.3578	0.6422
<u>11</u>	1	0.9988	0.0012
	2	0.0076	0.9924
	3	0.5138	0.4862
	4	0.4902	0.5098
<u>22</u>	1	0.9935	0.0065
	2	0.0063	0.9936
	3	0.6068	0.3931
	4	0.4607	0.5393

$d \approx 1$ for one moiety indicates localized excitation,
 $d \approx 0.5$ for both moieties indicates delocalized excitation

Table 3. Analysis of Electron Transitions according to eq. 3.2.7

Nr. of Compound	Transition O→I	Partial distances	
		for subunits left	right
<u>1</u>	1	112	343
	2	19	538
	3	68	472
<u>2</u>	1	59	59
	2	59	59
<u>3</u>	1	2	117
	2	15	109
	3	67	11
<u>4</u>	1	65	8
	2	83	96
	3	72	62
	4	90	66
	5	72	70
<u>7</u>	1	12	112
	2	0	118
	3	104	19
<u>10</u>	1	8	117
	2	155	24
	3	141	114
<u>11</u>	1	8	98
	2	154	28
	3	158	196
<u>22</u>	1	10	127
	2	111	7
	3	75	84

A small value for one and a high value for the other subunits indicate localization; nearly equal values for both subunits indicate delocalization of the excitation

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