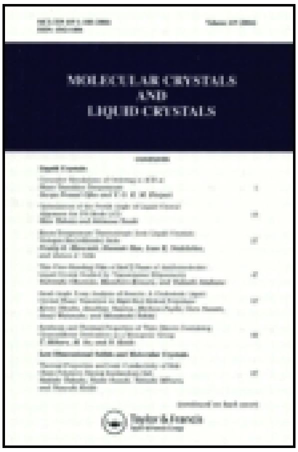

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Conformation Analysis and Absorption Properties of Anthraquinone Dyes—A Quantum-chemical Approach

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CONFORMATION ANALYSIS AND ABSORPTION PROPERTIES OF ANTHRAQUINONE DYES - A QUANTUMCHEMICAL APPROACH

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Abstract For a series of anthraquinone dyes the excited state properties are discussed as a function of the molecular conformation by using semiempirical INDO-MO calculations. It is demonstrated that the absorption maxima depend on details of the geometry as, e.g. inner hydrogen bridges and different substituents at the aromatic framework. In most of the cases the transition moment of the VIS absorption band has a strong component parallel to the long molecular axis, a result, which is important for practical use in display technology. The polarization of the electronic transition is strongly dependent on the position of the substituents at the anthraquinone core and the nature of these groups itself, too.

INTRODUCTION

Orientational Order

In display technology guest-host systems with high dye order parameters and large dichroism[1-3] are necessary to achieve a large contrast ratio between the on- and offstate. This ratio is influenced by the dye's concentration and the value of the extinction coefficient[4-6]. In the present work we discuss calculated electronic transition energies of selected anthraquinone dyes by using a semiempirical MO model in the Intermediate Neglect of Differential Overlap approximation. The knowledge of the crystallographic data[7-11] of some representative molecules allows the evaluation of common structural features. A comparison of calculated values with the experimental data obtained by UV/VIS-spectroscopy can lead to a first suggestion of possible *dye conformations and inner molecular* structural arrangements.

A single molecule with internal cartesian molecular axes x, y, z can be described by externally fixed device axes u, v, w using the Euler angles Φ, θ, ϕ (Figure 1). For a sufficient description of the statistical distribution of all molecular orientations in relation to the axes u, v, w the orientational distribution function $f(\Phi, \theta, \phi)$ has to be introduced. In the standard description of a nematic phase showing axial or more realistic cylindrical[12] symmetry with a director $\underline{n}$ there is only a dependence of f with the angles Φ and θ. The orientational order of nematic liquid crystals is in general specified by the Saupe order matrix S_{ij} with $i,j = x, y, z$. A diagonalization leads to two independent elements S and D, which fully describe the orientational order (Eq. 1 and 2)[13].

$$S = S_{zz} = \langle 0.5(3\cos^2\theta - 1)\rangle \tag{1}$$

$$D = S_{xx-yy} = \langle 0.5\sqrt{3}\sin^2\theta\cos 2\phi\rangle \tag{2}$$

S means the average deviation of the long molecular axis from the director and D means the difference in tendency of the two orthogonal axes of the molecular frame to align parallel to the director. For application in displays the macroscopic or optical order parameter S_{op}[13] is of fundamental interest. S_{op}, measured by linear dichroism can be described by Eq. (3), where α

$$S_{op} = 0.5(3\cos^2\alpha - 1) * S + 0.5\sqrt{3}\sin^2\alpha\cos 2\beta * D \quad (3)$$

and β specify the direction of the dipole transition moment vector in the molecular frame (Figure 1). If $D \neq 0$ the molecules show molecular biaxiality. Different theories concerning asymmetric liquid crystalline or dye orientational distribution were

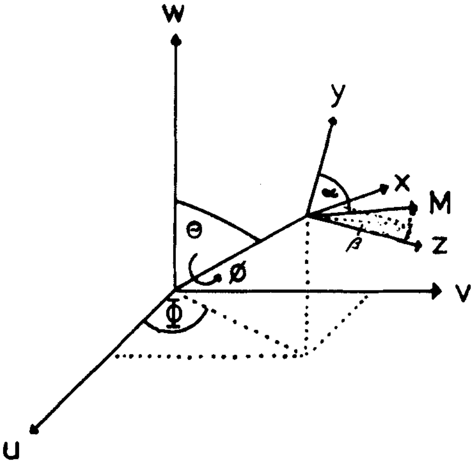

FIGURE 1 Orientation of the transition moment M in the molecular cartesian coordinate system and definition of the molecular axes x, y, z relative to the laboratory axes u, v, w.

developed[13,14]. The introduction of a biaxiality parameter allows to describe the deviation of the potential of mean torque, which is influenced by the solvent[14], from cylindrical symmetry. Asymmetric substituted anthraquinones have to be considered as dyes with molecular biaxiality. Therefore the biaxial order parameter D cannot be neglected. Figure 2 shows the used molecular axis definition for anthraquinone dyes, the labelling of the substituents and a general representation of the commercial D-series dyes (Merck Ltd., Poole, U.K.). In the case of asymmetric substituted anthraquinones the individual molecular long axis L lies in the x, z plane and a difference in the direction of the electronic transition dipole moment M and L occurs.

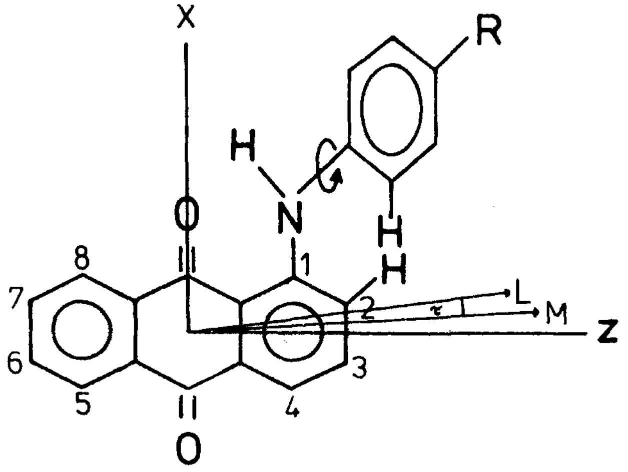

FIGURE 2 Definition of the axes x, z, M and L, labelling scheme in anthraquinone and structural features of the D-series dyes.

Electronic Absorption

The above mentioned transition moment of absorption is defined as:

$$\underline{M} = -e \int w_{(i)}{}^{*}\ r\ w_{(o)}\ dt \qquad (4)$$

$w_{(i)}{}^{*}$ and $w_{(o)}$ are the wave functions of the excited and the ground state, r is the electronic dipole moment operator (Eq. 4). A π-π^{*} transition is only possible if the direct product of the ground state wave function, the excited one and the dipole moment operator contains the totally symmetric representation. The transition probability is usually characterized by the oszillator strength, which is related to the integrated intensity of the absorption band.

Two of the transitions in the UV-region of the anthraquinone core are polarized parallel to the z-axis (324, 252nm) and the two others parallel to the y-axis (272, 249 nm)[3,15]. These four basic electronic transitions are found for all substituted anthraquinone dyes. For simple anthraquinone derivatives with substituents like NO_2, Br, or OH some rules concerning the polarization of the electronic transition can be given: Substitution in α-position (1,4,5,8) generally leads to one or two additional π-π^{*} transitions in the VIS-region[3]. The polarization of these bands is along the z-axis or includes a small angle with the z-axis in the yz-plane[15-17]. The introduction of substituents in the ß-position (2,3,6,7) of the anthraquinone core results in larger angles ß related to the z-axis or angle τ related to the long molecular axis L. For N-phenyl-substituted anthraquinones (D-27, D52M, D-35) (Figure 2) the dihedral angle σ between the normals perpendicular to the phenyl ring and the anthraquinone plane, obtained by X-ray single crystal analysis[9-11], is about 70°. The value of σ in solution is in general unknown and can influence the energy of the electronic transition.

In the crystalline state all α-substituents with bound hydrogen atoms like -OH or -NHR form asymmetrical hydrogen bridges with the neighboring carbonyl oxygen. A dilute solution of these dyes with an assumed solvation symmetry of the neighboring solute molecules[13] in the l.c. matrix should show a greater tendency in forming a symmetrical hydrogen bridge as found in the gas phase. This behavior should be caused by the lack of packing effects.

EXPERIMENTAL

The calculations, starting from crystallographic data, were done by using a semiempirical INDO molecular orbital approach[18], which has been written to reproduce one-electron properties (ionization potentials, electronic transition energies) with reliable accuracy[19]. In the subsequent CI-calculations a 15*15 array has been used to have acceptable CPU-time. The following data were calculated:

a) The excitation energies calculated by means of the above Configuration Interaction method.

b) The polarization of the transition. The angle τ was calculated by simple vector geometry using this polarization vector and the individual long molecular axis.

c) The oscillator strenghts of the transitions.

The dyes used for our studies are shown in Table I. The long molecular axis of all dyes is defined as the straight line between the greatest C-C distance in the molecule, except compound 2ClA, where the longest C-Cl distance was considered. Therefore the long axis of the dyes with small substituents (AA, ClA, CNA, A2A, H2A) is

TABLE I Anthraquinone dyes investigated (see also Figure 2).

Dye	R1	R2	R4	R5
AA	NH_2	H	H	H
ClA	Cl	H	H	H
CNA	CN	H	H	H
2ClA	H	Cl	H	H
A2A	NH_2	H	NH_2	H
H2A	OH	H	OH	H
D-35	NH-(p-Et)C_6H_4	H	H	NH-(p-Et)C_6H_4
D-52M	NH-(p-NMe_2)C_6H_4	H	H	H
D-27	NH-(p-NMe_2)C_6H_4	H	OH	H

nearly identical with the molecular z-axis, whereas for the dyes of the D-series an angle of about 30° between the long axis L and the z-axis is observed using crystallographic data[9-11]. The equipment used for the measurements in the UV/VIS-region as well as the preparation of the guest-host systems were described elsewhere[20,21].

RESULTS AND DISCUSSION

Existence of Symmetric Hydrogen Bridge in Anthraquinone D-Dyes

In a series of calculations the local structure of the inner hydrogen bridge has been investigated. In the crystalline state this hydrogen bridge is strongly asymmetric, in the gas phase or in solution the asymmetry should be reduced. A preference of symmetric hydrogen bridges has been suggested first by Pauling[22].

The optimized bridge distance is shown in Figure 3 for the dye AA. This arrangement is quite similar to all investigated dyes. The $O_C \cdots H{-}O{-}$ systems show minimal energy at a distance of 1.27 Å, whereas $O_C \cdots H{-}N{-}$ systems posses this minimum at 1.32 Å. The most probable hydrogen bridge type for isolated anthraquinone dyes with $O_C \cdots N$ and $O_C \cdots O$ distances of 2.62 Å and 2.51 Å is a nearly symmetric arrangement of the hydrogen atom between the two active centers, the carbonyl oxygen and the substituent in the 1-position[23]. The angle at the hydrogen bridge is between 160° and 170°. This is in agreement with an earlier investigation of some other anthraquinone derivatives[24], where the symmetric structure was the most probable suggested too. In consideration of a dilute dye solution in a l.c. phase

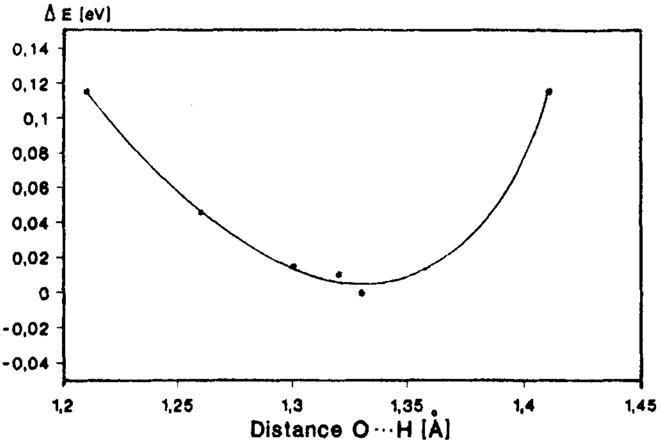

FIGURE 3 Relative energy of dye AA as a function of the distance $O_C \cdots H$.

like CB5 or PCH7, the electronic environment around the relevant region of interest should not disturb the symmetric arrangement of the hydrogen bridge intensely. This assumption is supported by the fixed conformation of the involved centers at the dye core and a symmetric solvation[13]. Results of calculations concerning the influence of the dihedral angle σ on the total energy are shown in Figure 4 for the dye D-52M. A simple potential function with an energy minimum at σ = 90° can be seen. Remarkable changes in the total energy occur at angles lower than 60° or higher than 120°, because two hydrogen atoms of the two different rings - the one in position 2 at the anthraquinone and the other in o-position to the amino function in the phenyl ring (Figure 2) - are closer than 2.4 Å (the van der Waal's radius of one hydrogen atom is 1.2 Å). Then the repulsion forces increase rapidly with increasing deviation from 90°. The energy difference between the calculated 90° geometry and the crystallographically realized 70° conformation[9,11] is about 0.2 eV (20 kJ/mol). This number is in an order of magnitude which can be provided by packing effects. Therefore a dihedral angle σ close to 90° in the l.c. phase is a realistic value.

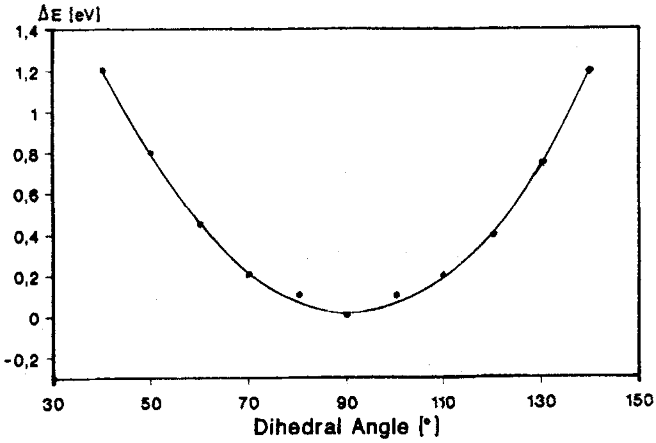

FIGURE 4 Relative energy as a function of dihedral angle σ for dye D-52M.

Electronic Transition Properties

One main question of interest is the solvent's influence on the electronic density distribution and one-electron energies in the dye molecule and the resulting changes in the absorption behavior. As the relative dielectric constants of the l.c. phase are always smaller than 10, and under the assumption of a rather symmetric solvation by the l.c. solute[13] the absorption quantities in the gas phase and in a dilute solution should be comparable. Therefore a comparison of the calculated data with those in an anisotropic solvent like CB5 or PCH7 may lead to first suggestions concerning the dye structure in a guest-host system. In Table II the calculated transition wavelengths of the dyes are presented together with the experimental data in the liquid crystalline phase CB5 and - some of them - in PCH7[25]. The comparison shows a

TABLE II Calculated and experimental absorption maxima.

Dye	calc. λ_{max}[nm];	exp. λ_{max}[nm]
AA	473	475
A2A	535	545
H2A	468	480
D-35	549	554
D-52M	537	546
D-27	578	595

Dye	calc. λ_{max}[nm];	exp. CB5 λ_{max}[nm],	PCH7 λ_{max}[nm]
ClA	356	334	338
CNA	375	320	316
2ClA	356	318	322

reliable agreement between the calculated and the experimental values. In many cases the maximum deviation is only about 20 nm. Only for the dyes ClA, CNA and 2ClA the difference increases up to 50 nm. Other authors described deviations between calculated and experimental values up to 100 nm or larger[15,16,24] using the averaged Pauling values for the distances and bond angles[22] in different calculation methods. But in all molecules with the above mentioned hydrogen bridge the calculated values are lower than the experimental one. Despite of the semiempirical character of the calculation method the difference of the transition energies can be semi-quantitatively explained, because the carbonyl function acts as a donor for inner molecular hydrogen bridges. This results in a hypsochromic shift[26]. Small deviations from the assumed symmetric inner hydrogen bridge show a negligible influence on the position of the main absorption band in the VIS-range, whereas larger distortions to shorter or longer $O_c\cdot\cdot H$ distances cause a shift of the absorption maximum to higher frequencies i.e. energies. This is presented for dye AA as an example for

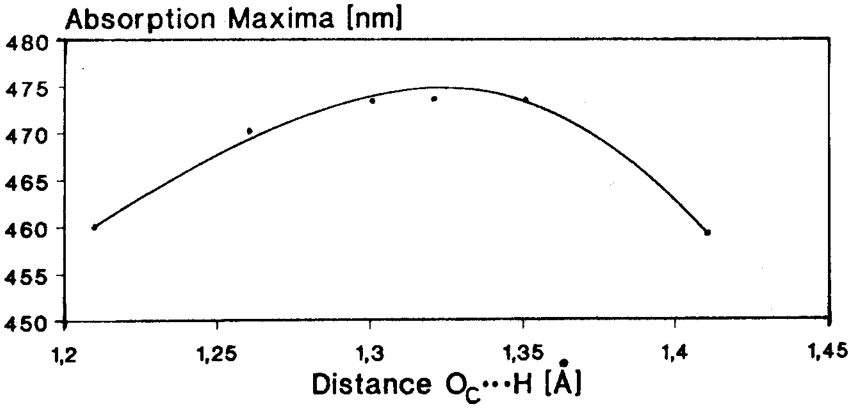

FIGURE 5 Absorption maximum of dye AA as a function of the distance $O_c\cdot\cdot H$.

all investigated dyes in Figure 5. Therefore the existance of inner molecular, nearly symmetrical hydrogen bridges is quite realistic.

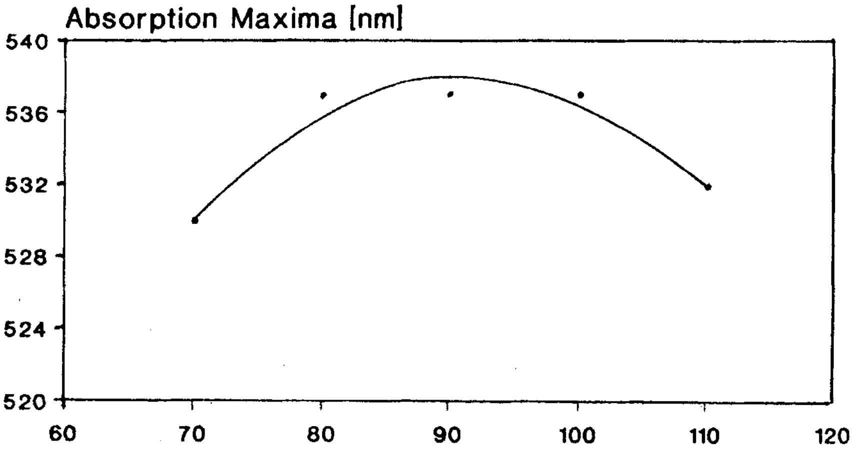

FIGURE 6 Absorption maximum of dye D-52M as a function of the dihedral angle σ.

The second question of interest is the influence of the dihedral angle σ on the spectral properties of the dyes. Figure 6 shows this dependence for dye D-52M. The absorption maximum is nearly constant in the range of the σ-angle from 70° to 110°. This result points out that the dihedral angle has only a small influence on the absorption maximum. Therefore the anthraquinone core and the phenyl ring can be considered as electronically isolated systems.

The third point of interest is the direction of the transition polarization relative to the long molecular axis in the VIS-region. The polarization of the electronic transition moments of the dyes has been calculated. The resulting angles τ between the transition polarization moment vector $\underline{M}$ and the long molecular axis L (Figure 2) are listed in Table III. In case of

TABLE III Angle τ between transition moment M and long molecular axis L

Dye	τ[°]
AA	11
A2A	0
H2A	0
D-35	12
D-52M	13
D-27	6
ClA	1
CNA	2
2ClA	54

symmetrical 1,4-substitution τ ≈ 0[15,16]. For all asymmetric substituted moment vector M and the long molecular axis L (Figure 2) are listed in Table III. In case of symmetrical 1,4-substitution τ ≈ 0[15,16]. For all asymmetric substituted anthraquinone dyes the angle between the transition moment and the long molecular axis is small except for the dye with the chlorine function in the 2-position.

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