Forschung, Wissenschaft

The Absorption Colour of Organic Azo Compounds *

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Abstract

Quantum chemical methods permit one to reveal scope and limitations of composite-molecule models formerly proposed to rationalize the absorption behaviour of azo compounds in the visible region. In order to give a justification of these approaches PPP-type many-electron wave functions have been subjected to "configuration analyses". The genesis of the colour-determining low-energy excited states has been followed within the framework of the Longuet-Higgins/Murrell method. The position of colour bands of various organic azo compounds are considered to support theoretical conclusions.

Introduction

The theory of "colour and constitution" of organic compounds can now be traced back for more than 100 years. It embraces various phenomenological conceptions which may roughly be classified into two distinct approaches. One of them emphasizes the whole delocalized conjugated system as being the chromophoric system. The second approach tries to give a rationalization in terms of chromophoric subsystems. Each of these approaches may be advantageous. The choice among them depends on the type of comparison that is wanted. The replacement of one or several atomic groups (e.g. =CH–) by other ones (e.g. =N–) without alteration of the extension of the conjugated system can be considered as perturbation of the whole, whereas attachment of substituents or elongation of the conjugated system may be better unterstood in terms of molecular fragments.

Quantum chemical methods revealed the nature of fundamental chromophoric systems owing their colour to low-energy $\pi\pi^*$-excited states. This has been formerly done by simple one-electron approximations, e.g. in the framework of the MO-FE theory (*Kuhn* [1], *Platt* [2]) or of the MO-LCAO theory (*Dewar* [3]). Furthermore, it has been shown to treat the phenomenological approaches theoretically both in viewing the chromophoric π-system as a whole or by dividing it into proper subchromophores. In doing this Dewar's perturbational treatment (PMO-theory) has turned out to be an extremly powerful tool. This subject has been discussed in former reviews [4].

The refinement of the π electron theory during the last two decades (including the electronic interaction) has brought about tractable computational methods which permit the calculations of absorption data of any electronic system. For this purpose the Pariser-Parr-Pople (PPP) method [5] has been widely used. Although the necessity of achieving reliable numerical data should not be questioned, one striking disadvantage of these calculations is rather obvious: More sophosticated methods inevitably overestimate each individual system under study making it thus difficult to gain easily more general conclusions. Since the theory of colour and constitution, in contrast, aims at a broad understanding of the absorption colour in terms of the chemical language rather than at a serious physical interpretation of individual phenomena, the more sophisticated and highest-level quantum chemical calculations on chromophores hardly stimulate chemical intuition. From this point of view it seems necessary to find theoretical methods which permit better understanding of the theoretical results obtained by the last-mentioned methods. Therefore, we should look for mathematical counterparts of concepts currently used in chemistry.

In this respect, it is worth mentioning that Baba, Suzuki and Takemura have shown more recently how to interpret electronic states of any π-system derived by refined quantum chemical methods either in terms of states of related iso-conjugated systems or in terms of states defined by molecular fragments [6]. The so-called "configuration analysis" provides criteria of the suitability of the distinct simplifying approaches and modes of interpretative power and can indicate, thus, the most appropriate reference system. In particular, this procedure reveals the various kinds of heuristic meaningful "building block models", whose application seems, at first sight, to be rather questionable in the case of a delocalized π-electron system.

If we have achieved a justification for any composite-molecule approach, we need a proper theoretical method to develop the many-electron wave functions in terms of the localized picture. A suited refined composite-molecule method was already created by *Longuet-Higgins* and *Murrell* [7] during the fifties (LHM method). A generalized version has been presented more recently [8]. However, it is well known that this method cannot compete with the above mentioned PPP method with respect to the numerical accuracy

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and may even completely fail, if the number of the presumed electronic configuration is too low (cf. for example ref. [9]). But if the configurations are appropriately chosen, taking into account the results of the configuration analysis, this approach is rather instructive. Since the theoretical expressions can be expanded into terms of the simple molecular orbital model some fundamental knowledge about the molecular orbitals of the fragments permits one to draw qualitative conclusions. This can easily be done by the aforementioned PMO theory of Dewar.

In this paper spectral absorption of various organic azo compounds, especially those of deeply coloured azo disperse dyes, are regarded from the viewpoint of building block models.

Theoretical Description of the Electronic States

Refined π approximations such as the PPP method provide many-electron wave functions which describe the ground and the lowest-energy excited states by the π system as a whole. The wave functions involve all the electrons which belong to the conjugated system. These functions are termed here by Ψ_0, Ψ_1, Ψ_2 etc. They are defined with the aid of delocalized molecular orbitals.

An alternative approach consists in defining many-electron functions by means of the fully localized orbitals of the molecular fragments. These wave functions involve the *no-b*ond *(NB)* configuration Γ_0 and *l*ocally *e*xcited *(LE)* configurations $\Lambda_{i\to j}$, where i indicates occupied molecular orbitals an j unoccupied molecular orbitals of the molecular subsystem. The junction between the fragments is taken into account by a third type of configurations, the so-called *c*harge *t*ransfer *(CT)* configurations $T_{k\to l}$. The molecular orbitals i and k now belong to different subunits. The latter approach corresponds to the chemical thinking in terms of local building blocks. In order to attain a simple and clear-cut interpretation the number of configurations (building block) should of necessity be restricted.

The configuration analysis permits one to judge to what extent any wave function Ψ_0, Ψ_1, Ψ_2 etc. can be described by wave functions of the types Γ_0, $\Lambda_{i\to j}$ and $T_{k\to l}$. Due to the fact that electronic states are less well described by means of localized than by delocalized molecular orbitals the correspondence between both sets of many-electron wave function is restricted. More exactly spoken, the expansion of the wave function Ψ in terms of a limited number of locally defined wave functions according to Equ. 1 is incomplete.

$$\Psi \approx c_0\ \Gamma_0 + \sum_{i\to j} c_{i\to j}\ \Lambda_{i\to j} + \sum_{k\to l} c_{k\to l}\ T_{k\to l} \qquad (1)$$

That means that the sum of the squared coefficients is less than unity. Thus the sum (denoted by r_M) indicates the adequacy of the model presumed. As long as the wave functions are described by a mixture of only a few configurations we get a clear picture about the nature of the electronic states. Provided that the wave function of the ground state *(G)* is nearly solely defined by the NB configuration Γ_0 the nature of the excited states indicates, at the same time, the nature of the corresponding transitions. In this case a transition can be either predominantly localized at one of the fragments or can be predominantly determined by CT configurations.

In order to understand the results of the configuration analyses we consider the genesis of these results within the framework of the LHM method. This method, which consists in calculating the coefficients of Equ. 1 by a separate energy minimization within a variation procedure, starts from the energy levels of the various configurations and the interaction terms between them. The energy of the lowest CT configuration is mainly determined by the first ionization potential and the electron affinity of the corresponding fragments. Due to a Coulombic interaction the energy of these states is lowered if both parts approach each other. The change in energy may be weakend or strengthened with increasing overlap between the subunits. The interaction between the CT and the NB configuration increases with the overlap of the highest occupied MO (HOMO) of the donor (D) and the lowest unoccupied MO (LUMO) of the acceptor (A) fragment, thus giving rise to an increase of the CT-type excited state with respect to the electronic ground state. On the other hand, the interaction term between CT and LE configuration is large, if either the occupied donor orbitals or the unoccupied acceptor orbitals of both molecular parts considerably overlap. A strong overlap may occur if the expansion coefficients of the relevant orbitals are large in the joined positions. In the case the LE configuration is less energetic than a CT configuration, the first one is stabilized by the CT excited state. Similarly, the energy of a low-lying CT configuration may be lowered by a LE configuration of higher energy. Many dyes owe their deep colour to transitions to excited states having either predominantly CT character (intramolecular CT-transitions) or predominantly LE character (local transitions, local chromophores). CT transitions have only non-zero transition probability if some overlap is guaranteed. The overlap should, however, not be very large. Due to mixing between the CT and the NB configurations the ground state attains CT character, which is accompanied by a lowering of its energy ("ground state depression"). If this energy splitting becomes very strong, the compound cannot display a deep colour, in spite of low-energy zero-order CT-configurations.

A remarkable change in colour may also be observed when two equal chromophores are brought together. Even in the absence of any overlap between both subunits energetic splitting occurs between the lowest-energy LE levels. This result from an interaction term between the zero-order LE-configurations (LE states)

which is of Coulombic nature (interaction between "transition densities"). As formerly shown by the molecular exciton theory [10], a more intense absorption at longer wavelengths should be observed with respect to the monomer, if the transition moments of the colour-determining transitions are approximately aligned in a head-to-tail arrangement. To get deeper understanding of the physical background of the refined composite-molecule methods briefly outlined above two excellent textbooks [11] might be consulted.

Application of 'Molecules in Molecule' Models to Organic Azo Compounds

Azobenzene and Related Compounds

The chromophoric system of azobenzene attracted much interest and PPP-type calculations provided a satisfactory interpretation of its spectral absorption curve in the ultraviolet and visible region [12, 13].

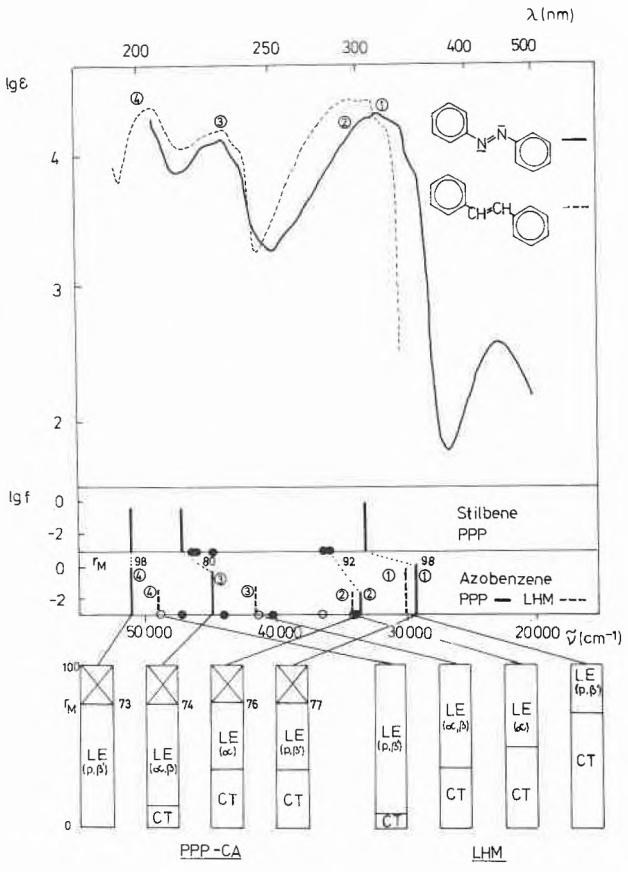


Fig. 1: Interpretation of the absorption spectrum of azobenzene according to PPP-CA calculations with respect to stilbene and, alternatively, with respect to the benzene-azobenzene composite-molecule, and results of the LHM calculation. The predicted electronic transitions are represented in bar-graph format (full bars: PPP, dotted bars: LHM), their oscillator strengths f being given in the left-hand scale. The numbers indicate r_M values in %. The configuration mixing of significant excited states according to both the PPP-CA and LHM calculations is illustrated at the bottom.

Results are exemplified in Fig. 1 where theoretically derived $\pi \rightarrow \pi^*$-transition energies are depicted by bars superimposed on the experimental spectrum. The heights of the bars correspond to the theoretical oscillator strengths which, provided a comparable band width, are proportional to the molar extinction coefficients. The configuration analysis of azobenzene with respect to stilbene (cf. Fig. 1) shows the close correspondence of the most important electronic states of both systems. An alternative interpretation refers to molecular fragments within a benzene-azo-benzene unit representation (denoted by model *A* in Fig. 2). According to the low r_M values of the configuration analysis (cf. Fig. 1) the latter reference system is less suited. Inspite of this deficiency this approach leads to two important conclusions. First, one of the high-energy excited states is predominantly localized on the benzene fragments (similar results are obtained for stilbene) and, secondly, the lowest-energy state exhibits considerable benzene-to-azo CT-character. The same conclusion has been drawn from LHM calculations [13], whose results are indicated in Fig. 1 by dotted bars. In terms of the composite-molecule approach the intense colour-determining long-wavelength transitions arise, therefore, from two low-energy CT-configurations which effectively mix with the excitonic combinations of the locally-excited states of the benzene fragments.

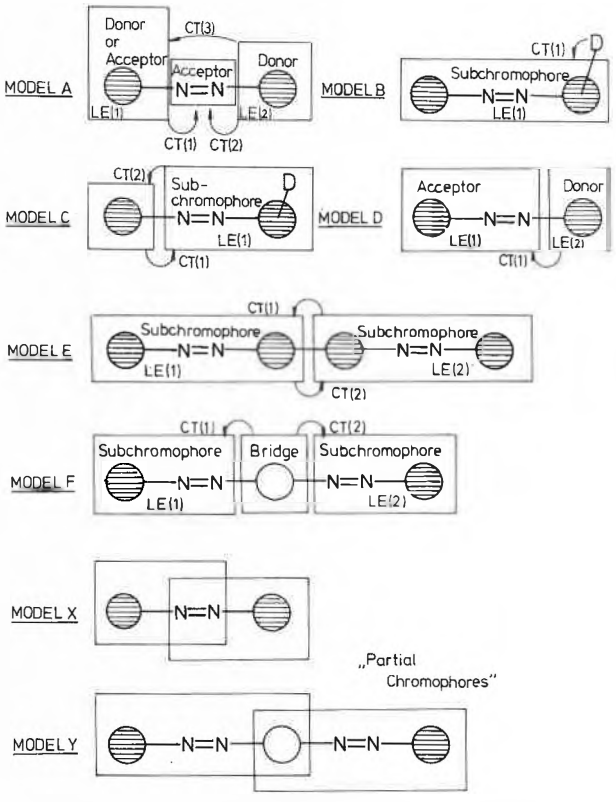
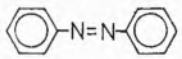
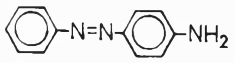


Fig. 2: Different fragmentation modes and denotation of important locally excited (LE) and charge transfer (CT) configurations defined by the resulting molecular fragments.

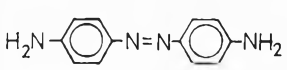
The lowest excited state migrates to lower energies the less energetic the CT-excitations are. Bathochromic shift consequently occur either by enlarging the acceptor power of the azo group (e.g. protonation of this group) or by replacing the benzene fragments by hydrocarbons with lower ionization potentials. Thus, in accordance with the descent of the ionization potentials, the absorption wavelengths of the colour band (first intense longest-wavelength absorption) increase in passing from azobenzene (316 nm) via 1,1′-azonaphthalene (371 nm [14]) to 9,9′-azoanthracene (476 nm [15]). Similarly red-shift has been observed in passing from azobenzene (I) to donor-substituted azobenzene, such as II.



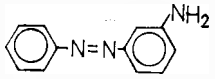
I: 318(4.34)
in ethanol[20]



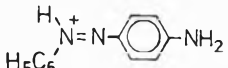
II: 384(4.37)
in ethanol[20]



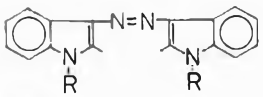
III: 399(4.50)
in ethanol[20]



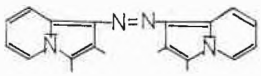
IV: ~420, 316(4.16)
in ethanol[20]



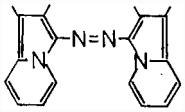
V: 500(4.09)
in ethanol/HCl[24]



VI: R=H 411(4.43) in ethanol[27]
R=Me 424(4.44) in methylene chloride[28]



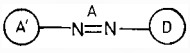
VII: 510(4.69)
in methylene chloride[29]



VIII: 568(4.79)
in methylene chloride[29]

Donor Substituted Azobenzenes and Related Compounds

Introduction of donor substituents gives rise to low-energy CT configurations which determine the long-wavelength absorptions of many important textile dyes. The red-shift depends upon the extent of lowering of the ionization potential of the benzene unit rather than upon the amount of charge transferred from the substituent to the benzene ring in the ground state. The observed sequence of increasing red-shift occuring by *para*-monosubstitution H < F < Cl < Br < J < SMe < OMe < NMe_2 [16] does, consequently, not follow the Hammett-type substituent constants. It correlates, however, closely with the first ionization potentials of the substituted benzenes [13]. Only slight bathochromic effect is observed in passing from p-monosubstituted to p,p′-disubstituted azobenzenes [17] (cf. II and III). In contrast to the traditional spectral resonance arguments the *meta*-monosubstituted aminoazobenzene(IV) absorbs at longer wavelengths than the *para*-isomers [18]. As according to model *A* or model *B* of Fig. 2 equal molecular fragments are involved, the different spectral properties are exclusively determined by the distinct positions of linkage. An effective mixing between the CT and LE configuration necessitates high coefficients in LUMOs of the fragments and, conversely, a small expansion coefficient in HOMO of the donor to avoid a substantial ground state depression. The *meta*-isomer satisfies this requirement better than the *para*-isomer (cf. Fig. 3).



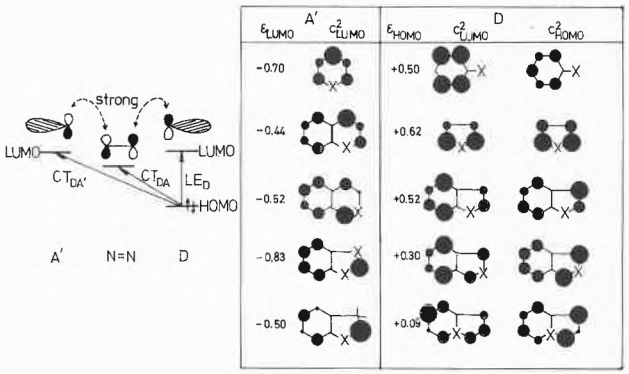


Fig. 3: MO energy levels of azo compounds bearing both donor (D) and acceptor (A′) fragments and schematic representation of the expansion coefficients of several subunits D and A′. The open (shaded) circle signifies that the positive (negative) lobe of the $2p_\pi$ orbital is above the molecular plane. Their areas indicate the magnitude of the squares of the expansion coefficients of the HUCKEL-frontier orbitals ($h_x = 1$, $k_{cx} = 1$).

A more detailed analysis of the relationships according to model *B* has shown [19], that the weak longest-wavelength absorption of IV corresponds to the second low-energy transition of I (cf. Fig. 1), whereas the strong longest-wavelength absorption of III corresponds to the intense lowest-energy transition of I. Similar considerations permit one to rationalize the effect of multiple donor substitution recently examined for methoxy-substituted azobenzenes [21]. According to these considerations appropriate multiple substitution may shift the colour band bathochromically up to the near infrared, but for similar reasons to those mentioned above the absorption intensity is low in many cases [19]. Strong long-wavelength absorptions occur, however, for substituted azobenzenes which exhibit some ground state stabilization. Substantial

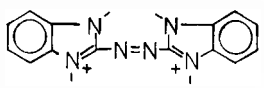
CT contributions to the electronic ground state in the presence of strongly electron-releasing donor groups, lead to some limitation of considerations according to model *A* and *B*. Comparison of the r_M-values of ground and lowest-excited states between azobenzenes and *para*-aminoazobenzenes, listed in Table 1, clearly reveals that in the latter case model *A* is less appropriate. The aminophenylazobenzene composite-molecule (model *C*) proved to be the more suited reference state. This result is completely equivalent with an intuitive picture suggested by the mesomeric approach (e.g. [22]) or by Dähne's polymethine conception [23]. Accordingly, the electronic structure of *para*-aminoazobenzene may be considered as approaching a polymethine bond system, characterized by a high extent of bond equalization and charge alternation. This case is realized more closely in the case of monoprotonated *para*-aminoazobenzene (V). As in polymethine dyes an intensive long-wavelength absorption has been observed for V.

The assumption of a fundamental aminophenylazo chromophore according to model *C* is also rather advantageous for rationalizing substituent effects at the phenyl group. It is well known that the attachment of substituents at the unsubstituted phenyl group of *para*-aminoazobenzenes acts predominantly as an inductive perturbation of the aminophenylazo chromophore [25, 26] mainly reflecting the electron density change at the substituted azo nitrogen. Bathochromic shifts occur with acceptor substitutions because the electron density increases at this nitrogen atom upon excitation to the lowest excited state. This model obviously loses its relevance if a second amino group is introduced in the p'-position giving rise to a symmetrical azo dye.

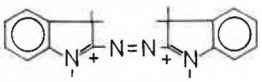
The considerations show that long-wavelength absorption can be obtained in two different ways by donor substitution: First, attachment of donor substituents to those positions which, due to an effective HOMO-LUMO interaction, give rise to a ground state stabilization and create a polymethinic subchromophore. These compounds display strong absorptions, but the wavelengths of these absorptions generally do not exceed those of the polymethine subchromophores. Secondly, attachment of the donor substituents to those positions which only give rise to a weak ground state stabilization, but cause an effective mixing of the LUMOs. In this case the composite-molecule structure of the azo compound is overwhelmingly retained. In contrast to the first case, however, the longest-wavelength absorptions should be weak.

This relationship can be pursued with heterocyclic azo compounds which contain five membered heterocyclic residues instead of the donor substituted benzenoid residue. The commonly used synthetic routes lead to compounds which possess some ground state stabilization, such as VI–VIII. They display intense long-wavelength absorptions giving rise to yellow, red or blue shades. Replacing the α-CMe group of the indole nuclei of VI by the more electronegative aza nitrogen leads to indazole compounds which, as expected, absorbs at shorter wavelength (λ 395 nm, lg ε 4.24 in acetonitrile) [28]. This effect of heteroatomic substitution is, however, overcompensated, if the indazole nuclei undergo additionally deprotonation, giving rise to a dianionic azo compound (λ 552 nm, lg ε 4.46 in dimethylformamide/ K-tert. butoxide). The indolizine derivatives VII and VIII owe their deep colour to the low ionization potential of the heterocycle. From the composite-molecule viewpoint absorption at even longer wavelengths might occur with appropriately substituted benzene fragments in the indolizine ring system (cf. expansion coefficients depicted in Fig. 3).

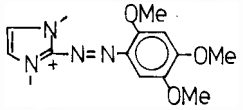
It seems more difficult, at first glance, to rationalize the deep colour of the dicationic azo compounds IX and X. The charges at the heterocyclic groups may suggest an acceptor type behaviour. However, PPP-CA and LHM calculations reveal consistently, that even in these cases heterocycle-to-azo CT-transitions are strongly involved into the lowest-energy electronic transitions. This feature results from the fact that the charges at the heterocyclic moieties significantly lower the LUMO energy of the azo group within the zeroth-order composite-molecule structure giving rise to sufficiently low CT-transition energies.



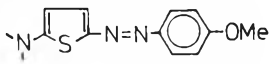
IX: 552(4.50)
in acetonitrile[29]



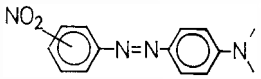
X: 625(4.58)
in sulphuric acid[29]



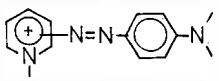
XI: 365(4.05) 489(4.37)
in water, pH 5 [31]



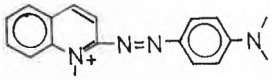
XII: 483(4.70)
in ethanol[42]



XIII: 2-NO_2 425(4.56)
4-NO_2 453(4.64)
2.4-di NO_2 491(4.58)
2.6-di NO_2 450(4.43)
2.4.6.-tri NO_2 520(4.68)
in methanol [34]



XIV a ortho 557(4.77) in acetonitrile[35]
b meta 458(4.47) in ethanol[36]
c para 555(4.48)



XV: 591(5.00)

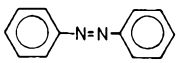
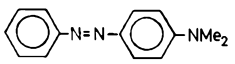
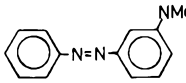
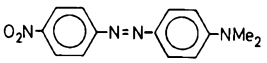
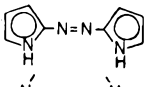
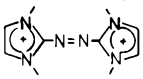
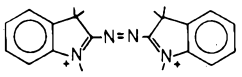
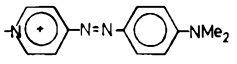
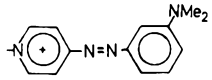
If the azo group bears two different donor groups two intense long-wavelength absorptions may appear. This has been observed for substituted azobenzenes [30] and heterocyclic azo compounds such as XI [31]. As two more or less energetically separated long-wavelength transitions are already expected for many symmetric compounds, the appearence of a second absorption band does not necessarily reflect two independent local excitations (so-called "partials" [32] or excitations in "quasiautonomic systems" [33] according to model *X*). According to our calculations both of the long-wavelength absorptions of XI are solely determined by the benzenoid fragment.

Donor-Acceptor Substituted Azobenzenes and Related Compounds

An important type of azo compounds contains a donor as well as an acceptor residue. Examples are appropriately substituted azobenzenes such as XIII or heterocyclic azo compounds such as XIV.

According to PPP-CA calculations (model *A*) the CT-transition from the donor part to the azo group

Table 1: Results of configuration analyses for the ground state Ψ_0 and the lowest excited state Ψ_1 with respect to models explained in Fig. 1 (data given in %)*

Compound	Model	*N*	Electronic State $\pi\pi^*$	r_M	Total Weight of Dominant Lowest Energy Configurations				
					NB	LE**	CT(1)	CT(2)	CT(3)
	*A*	5 × 5	Ψ_0	92	72	–	7	7	–
			Ψ_1	77	–	44	18	18	–
	*A*	5 × 5	Ψ_0	87	69	–	5	9	1
			Ψ_1	65	3	13	8	28	7
	B	5 × 4	Ψ_0	90	74	–	12	–	–
			Ψ_1	77	5	21	44	–	–
	C	5 × 5	Ψ_0	95	85	–	9	–	–
			Ψ_1	88	–	63	9	12	–
	*A*	5 × 5	Ψ_0	87	72	–	6	7	–
			Ψ_1	76	1	19	7	44	–
	B	5 × 4	Ψ_0	93	77	–	14	–	–
			Ψ_1	82	–	25	47	–	–
	*A*	6 × 6	Ψ_0	86	68	–	4	10	1
			Ψ_1	63	5	10	6	22	13
	D	5 × 5	Ψ_0	88	79	15	43	–	–
			Ψ_1	67	7	48	25	–	–
	*A*	5 × 5	Ψ_0	88	69	–	9	9	1
			Ψ_1	64	–	12	21	21	3
	*A*	4 × 5	Ψ_0	86	70	–	7	7	1
			Ψ_1	66	–	20	19	19	4
	*A*	4 × 5	Ψ_0	73	58	–	6	6	1
			Ψ_1	61	–	25	13	13	5
	*A*	7 × 6	Ψ_0	89	52	–	–	17	4
			Ψ_1	59	22	4	–	6	19
	*A*	7 × 6	Ψ_0	93	62	–	–	12	2
			Ψ_1	71	1	5	–	29	30
XXIV	*E*	4 × 4	Ψ_0	93	92	–	1	1	–
			Ψ_1	84	–	73	6	6	–
XXV	*F*	6 × 6	Ψ_0	87	62	–	6	6	–
			Ψ_1	72	–	29	12	12	–
XXX	*C*	5 × 5	Ψ_0	94	79	–	12	–	–
			Ψ_1	81	–	74	–	9	–

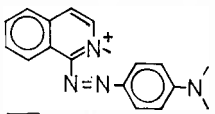
* The parametrization of the PPP-calculations is the same as formerly used [61]. Sixteen configurations have been employed in the PPP configuration interaction. The number of the configurations of the composite-molecule reference structure $N = n \times n'$ is given within the table, where n denotes the number of the upermost occupied orbitals and n′ the number of lowest empty orbitals. The sum of the squared expansion coefficients define the r_M values of each electronic state listed in the table.

** The locally-excited states of the molecular fragments undergo, in general, an excitonic-type splitting if brought together to real bond distances. For that reason the sum of local contributions is given.

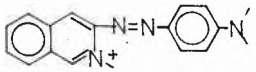
as well as from the donor part to the acceptor substituent contribute to the appearence of the colour band (cf. Table 1). Extremly long wavelength absorptions should occur if the electron affinity of A′ is high, the ionization potential of D is low and the overlap between the LUMO of all three A′, A and D is large (cf. Fig. 3). The consideration may be simplified if A′ and A are considered as a unit according to model *D*. In good agreement with experimental observations concerning the acceptor strength of A′ and A′–A, resp. the bathochromic shift is large if acceptor substituents are situated in the *para*- and *ortho*-positions (cf. XIII). This fact has recently been corroborated with absorption wavelengths of the various dinitrilo substituted aminoazobenzenes [37]. Appropriate substitution of azobenzene shifts the maximum of the colour band up to 655 nm [38] thus making available every shade between yellow and green.

The spectra of XIII and XIV, and of various other disperse azo dyes of this type [34, 39, 40] suggest the presence of low-energy CT configurations which do not only mix with locally excited states but also with the no-bond ground state. This, in turn, should be accompanied with some bond equalization via the azo group. For that reason XIV and related compounds might be considered as diazahemicyanine dyes rather than as typical azo dyes [41]. In sharp contrast to typical azo compounds several diazahemicyanines show a negative solvatochromism [35] and a negative halochromism [42, 43]. Both properties reflect the significant change in the electronic structure generated by the simultaneous presence of donor and acceptor group in different fragments [44]. The buildung unit model *A* attains, however, increasing validity in passing from the 4-dimethylamino-XIV to the 3-dimethylamino isomer (cf. Table 1). According to PPP calculations these compounds should absorb at significantly longer wavelengths, but with lower intensity in accordance with the strong CT character of the pertinent lowest excited state. This effect may be strengthened by appropriate multiple substitution [19].

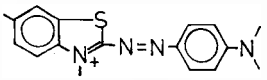
In spite of the fact that for reasons outlined above model *A* is not highly suited to treat the isomeric compounds XV–XVII, the different spectral positions of the colour bands may be qualitatively understood by model *A*: Thus the blue-shift in passing from XV



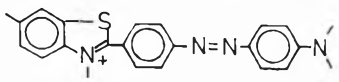
XVI: 570,5 (4.63)



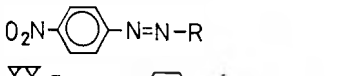
XVII: 537 (4.74)
in acetonitrile [35]

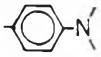


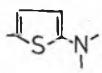
XVIII: 600



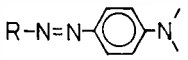
XIX: 481
in methanol [45]

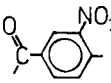


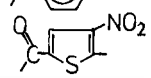
XX a R =  480 (4.52)

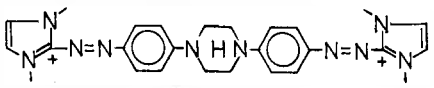
b R =  554 (4.70)

in ethanol [42]

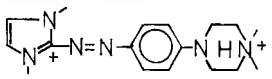


XXI a R =  485

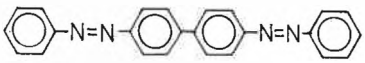
b R =  582 [46]



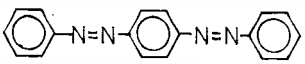
XXII: 540



XXIII: 482
in water, pH 5 [31]



XXIV: 364 (4.66)



XXV: 359 (4.64)
in ethanol [20]

to XVI reflects a decrease in electron affinity (cf. HOMO energy of the LUMO given in Fig. 3). The clearly distinguished absorptions of the isomeric compounds XVI and XVII, on the other hand, obviously result from the different strengths of the LUMO-LUMO interaction between the acceptor fragments.

An interesting spectral behaviour has been observed in passing from XVIII to XIX [45]. A superficicial assignment of both dyes to diazahemicyanines may suggest that XIX should be more bathochromic than XVIII: a hypsochromic shift has, however, experimentally been observed. It should be taken into account that insertion of a *para*-phenylene residue separates the two acceptor groups, and thus the CT donor-to-acceptor configurations can no longer interact. Moreover, due to the large intermolecular distance one of them becomes energetically unfavoured. As a consequence, the compound XIX is chromophorically more closely related to substituted aminoazo dyes than to heterocyclic dyes of the structure XVIII.

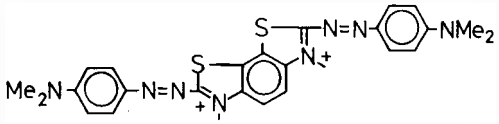
In order to attain deeply coloured compounds it is advantageous to replace a benzene ring by a thiophene ring, as exemplified by XX and XXI. Whereas the red-shift arising by substitution of 4-dimethylaminophenyl by the 5-dimethylamino-thienyl residue (XXa and XXb) may readily be explained by the

easier ionizability of the latter fragment, the red-shift accompanied by analogous substitution within the acceptor part in passing from XXIa to XXIb is less trivial. PPP-type calculations, which correctly reproduce the bathochromicity of XXIb, show that the aminophenyl-to-azothiophen CT configuration is more energetic than the aminophenyl-to-azobenzene CT configuration making it impossible to give the explanation in terms of CT-configurations. The origin of the longer-wavelength absorption of XXIb is the lower LE excitation energy of the thiophene residue in comparison to the iso-π-electronic benzenoid fragment.

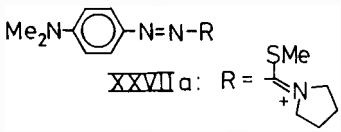
Bichromophoric Azo Compounds

In some cases it is advisable to consider azobenzene itself as a fundamental subchromophor (model *B*). This approach may be applied to treat the substituent effect (leading to the same conclusion as drawn above), but becomes especially important for understanding the spectral effects associated with the union of two (or several) azobenzenes or related systems. In the absence of an overlap between the component half structures the interaction should be of the excitonic type. Whereas no remarkable change occurs by joining two azobenzenes through an ethylene or methylene group [47] the expected shift to longer wavelength has been observed for the structurally fixed azo compound XXII with respect to XXIII. Conjugatively linked azobenzenes such as XXIV owe their red-shift in comparison to azobenzene to both the excitonic and the overlap effect. The same holds for symmetrically substituted benzidine bisazo dyes [47]. In the case of non-symmetrical dyes the excitonic type interaction is of less importance but the failing of a complete agreement between the spectrum of the benzidine azo dyes and for those of composites of the component half structures indicates the presence of a weak orbital p_π-overlap between the linked positions. This overlap has been excluded by introducing the 2,2′,6,6′-tetramethyl benzidine nucleus [48]. If the central unit is benzene (e.g. in XXV), naphtalene etc. the overlap is relatively strong and leads, therefore, to an complex melange of LE- and CT-configurations. There may be a similarity between the spectra of the composite-dye-molecule and that of parent structures defined by including the central group according to model *Y* [49]. This type of comparison works well in the case of 1,3-coupling by benzenes [49, 50] or 1,5-coupling by naphthalene [51], in contrast to 1,4-coupling and 1,7-coupling, resp. The same type of comparison has been employed for bisazo dyes which are joined through a heteroatomic bridge such as oxygen [52]. This splitting of the colour band of XXVI suggests the presence of an excitonic-type interaction between the two strong subchromophores in head-to-tail arrangement [53]. Comparing XXVI with XXVIa according to the model *F* the non-negligible CT effects of the central benzene unit can be demonstrated. Thus the dye XXVIIb, which comprises the benzene unit, also represents a more appropriate reference structure as XXVIIa (model *Y*).

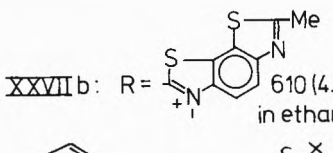
Finally, the azo compounds XXVIII to XXXI exemplify cases whose longest-wavelength absorptions are not determined by the azochromophore but only by the residues. The azo group is involved into the electronic excitation at shorter wavelengths. As well known appropriate joining of different chromophores leads to mixed dyes of new colour properties. A spectral study on green azo anthraquinone dyes showed that the absorptions of the constituent sub-chromophores are essentially retained [59]. The blue anthraquinone subchromophore and the yellow azo subchromophore retain much of their individuality, inspite of their conjugative junction. As far as both chromophores are



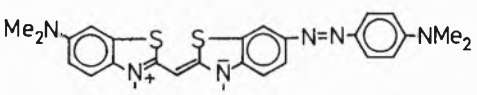
XXVI: 552(4.82) in ethanol [53]
660(5.07)



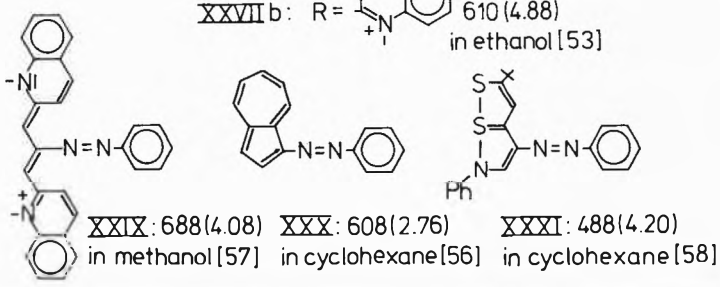
XXVIIa: R = 427(4.48) in ethanol [54]



XXVIIb: R = 610(4.88) in ethanol [53]



XXVIII: 424
513[55]



XXIX: 688(4.08) in methanol [57]

XXX: 608(2.76) in cyclohexane [56]

XXXI: 488(4.20) in cyclohexane [58]

joined through an amino group this group seems to be involved into the excitation of both chromophores according to model *X*, in close correspondence to former discussions on nitrodiphenylamine dyes [60].

In summary, quantum chemical methods provide arguments for deducing relations between colour and electronic structure in terms of local events. The adequacy of "molecules in molecule" models may be judged by "configuration analysis" of the wave functions of the total π-electronic system. Conclusions about the absorption colour can be drawn starting from the absorption behaviour of the subchromophores, their ability to accept or to release electrons and the strength of overlap between relevant molecular orbitals. Whereas the destructive configuration analysis of a system defines proper constitutive elements, the constructive LHM theory allows to express the behaviour of the system in terms of elements found by analysis. Investigations along this line may help to fill the gap between phenomenological and quantum chemical approaches. Thus a rough knowledge about quantum chemical approximations permits a better understanding of the absorption colour in terms of the chemical language and encourages to make predictions about the absorption behaviour of azo compounds being as yet unknown.

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