Monatshefte für Chemie 115, 21—34 (1984)

Monatshefte für Chemie
Chemical Monthly

What Is the Basic Chromophore of a Dye?

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(Received 8 June 1983. Accepted 29 June 1983)

Taking the 4,5-diphenyl-substituted 2-dimethylamino-3-azacyclopentadienone (**4**) as an example its colour has been discussed in relation to different basic chromophores (parent chromophores). The parent chromophore can be defined either as the structure which has nearly the same absorption wavelength as the dye under consideration or as the substructure which is electronically most closely related to the dye. In the case of **4** both considerations lead to different results. Based on the correlation diagram between the electronic states involved in the electronic excitation the long-wavelength absorption of **4** is better understood in terms of the merocyanine parent chromophore than in terms of a betainic substructure, which should have the same colour as **4** and is the parent chromophore according to *Klessinger*. This conclusion is drawn from *PPP* configuration analysis of the wavefunctions of **4** relative to different molecular substructures. The molecular geometry predicted by the geometry-optimized MINDO/3 and QCFF/Pi calculations provided additional arguments in favour of the cyclomerocyanine structure of **4**. In respect to the colour **4** belongs to a new series of cyclic-conjugated chromophoric systems.

(Keywords: Dye; Colour and constitution; Chromophore; Streptopolymethine; Computation; PPP; MIM; MOA; CA; FMO; MINDO/3, QCFF/Pi)

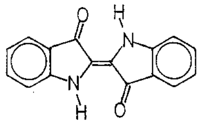
Was ist der Grundchromophor eines Farbstoffs?

Die Farbe des 4,5-diphenyl-substituierten 2-Dimethylamino-3-azacyclopentadienons (**4**) wird im Hinblick auf verschiedene Grundchromophore diskutiert. Der Grundchromophor kann entweder mit der Struktur identifiziert werden, welche die gleiche Absorptionswellenlänge wie die betrachtete Verbindung aufweist, oder mit der Struktur, welche elektronisch am stärksten mit dem Farbstoff verwandt ist. Im Falle **4** führen beide Betrachtungen zu verschiedenen Ergebnissen. Auf Grund des Korrelationsdiagramms der

Elektronenzustände, die in die Anregung eingeschlossen sind, wird die langwellige Absorption von **4** besser verstanden als Merocyaningrundchromophor, als durch eine betainische Teilstruktur, welche die gleiche Farbe wie **4** aufweisen sollte und nach *Klessinger* der Grundchromophor ist. Diese Schlußfolgerung wird aus der *PPP*-Konfigurationsanalyse der Wellenfunktion von **4** in bezug auf verschiedene molekulare Teilstrukturen gezogen. Die durch Geometrieoptimierung in MINDO/3 und QCFF/Pi-Näherung berechnete Molekülgeometrie lieferte zusätzlich Argumente zugunsten der Cyclomerocyaninstruktur von **4**. Bezüglich der Farbe kann **4** zu einer neuen Serie cyclisch-konjugierter Chromophore gerechnet werden.

Introduction

The knowledge of the parent chromophore (or "chromogen" according to Ref. [1]) of organic dyes is of great heuristic value. This has been demonstrated by *Klessinger* and *Lüttke*[2] who defined the parent chromophore of indigo **1**. According to *H*MO[2] and *PPP* calculations[3] of **1** and of fragments the benzene rings are not essential for long-wavelength absorption of indigo. A long-wavelength absorption has been predicted for the substructure indicated in formula **2**. Later this prediction was confirmed experimentally[5]. The compound **3** absorbs at only 118 nm shorter wavelength than **1** (in tetrachloroethane)[4].



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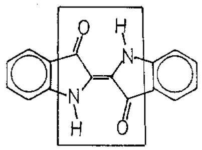

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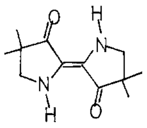

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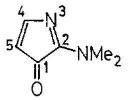
An alternative way in defining the parent chromophore consists in analyzing the electronic structure of the dye molecule with respect to different topologically and π-electronically equivalent reference structures[6]. These reference structures may be fragmented molecules (such as in **2**) or molecules in which one bond or several bonds of the dye molecule are broken. If a close correlation exists between the electronic ground states and the lowest-excited states of the dye molecule and those of the reference structure colour-structure relationship can be readily developed and well conceived in terms of this reference structure. Analysis of the results of the *PPP* calculations provides an objective criterion to how strongly the wavefunctions are correlated. According to this approach the parent chromophore is defined by that substructure which exhibits close correlations between the relevant electronic states. The absorption wavelength of basic chromophores defined along these lines may, however, differ more or less from that of the dye. Inspection of the wavefunction enables one to predict sufficiently any bathochromic shift which the colour band of the parent chromophore experiences upon structural change.

In the case of indigo, *Klessinger*'s consideration of the transition energy[2, 3] and our analysis of the wavefunctions[6] has led to the same parent chromophore. The H-indigo subchromophore of formula **2** absorbs not only at long wavelengths but also represents an appropriate basis for the theoretical derivation of the shift of the colour band associated with structural change.

The blue 4,5-diphenyl-substituted 2-dimethylamino-3-azacyclopentadienone (**4**) (described in Ref. [7]) affords, however, an example for which both approaches lead to different conclusions.



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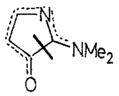

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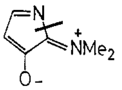

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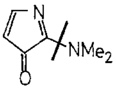

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According to *Klessinger*[8] the parent chromophore of **4** is not the merocyanine chain **5**, which differs from **4** by the absence of the bond between the atoms 1 and 2, because the structure **5** should absorb light at markedly shorter wavelengths than **4**. Breaking of the bond between the atoms 2 and 3, however, brings about a substructure **6** which absorbs at comparable wavelengths to **4**. With regard to the wavelengths, **6** should be the parent chromophore of **4**[8].

A third potential parent chromophore has not yet been considered. The dye **4** represents a substituted 3-azacyclopentadienone according to fragmentation mode **7**. As is well known[9] the related cyclopentadienones are coloured compounds.

The aim of this paper is to analyze the π-electronic states of **4** with respect to those of **5** to **7**. This is done by *PPP* molecular configuration analysis. The analysis will unequivocally answer the question as to which of the reference structure is electronically best related to **4**. In addition, the results of the calculation of the molecular geometry of **4** and its implications concerning the absorption wavelengths are discussed.

Computational Method

The electronic transition energies are calculated by the conventional *Pariser-Parr-Pople* (*PPP*) method[10] which has proved an invaluable tool in calculating the position of the absorption bands of organic dyes[11]. A standard procedure was employed in this paper within the fixed β approximation using the *Mataga-Nishimoto* relationship[12] for the two

Table 1. *Calculated and experimental transition energies of 2-dimethylamino-3-azacyclopentadienone* (**4**)

Method	Type	Calculated transition energy (μm^{-1})	Oscillator strength
PPP/1[a]	$S_0 \rightarrow S_1$	1.64	
	$S_0 \rightarrow S_2$	2.99	
	$S_0 \rightarrow S_3$	4.25	
PPP/2[b]	$S_0 \rightarrow S_1$	1.36	0.03
	$S_0 \rightarrow S_2$	3.67	0.53
PPP/3[c]	$S_0 \rightarrow S_1$	1.67	0.04
	$S_0 \rightarrow S_2$	3.84	0.50
QCFF/Pi[d]	$S_0 \rightarrow S_1$	1.88	0.02
	$S_0 \rightarrow S_2$	4.21	0.29
Experimental results		1.68 (3.35)[e, f]	
		2.96 (4.20)	
		3.82 (4.19)	

[a] DCI approximation. The S_3 state of the *PPP*/1 calculation corresponds to the S_2 states of the *PPP*/2 and *PPP*/3 calculation (cf. text).

[b] SCI approximation, idealized geometry and standard parametrization.

[c] SCI approximation, idealized geometry and consideration of the long CC bond length between the atoms 1 and 2 (156 pm) by the resonance integral β_{12} ($\beta_{12} = -1.707$ eV) according to Ref.[26].

[d] Based on fully optimized geometry of the QCFF/Pi calculation.

[e] Transition energies (lg ε) of 2-morpholino-4,5-diphenyl-3-azacyclopentadienone in acetonitrile.

[f] According to the *PPP*-calculation of 2-dimethylamino-4,5-diphenyl-3-azacyclopentadienone the most intense absorptions below 5.0 μm^{-1} should occur at 1.88, 3.02 and 3.92 μm^{-1}. Thus, the second absorption band is due to singly-excited states of the π-electronic system rather than to doubly-excited states, as suggested by the *PPP*/1 calculation.

center repulsion integrals. The configuration interaction treatment involved either all singly and doubly excited configurations (DCI) or all singly excited configurations (SCI). As long as is not otherwise stated an idealized geometry has been employed (regular pentagon, all bond lengths equal to 140 pm except of the CO bond, which was fixed at 122 pm).

The parameters of the SCI approximation are chosen as follows: U_C: -11.42 eV, $U_{N(aza)}$: -14.16 eV, $U_{N(amino)}$: -21.22 eV, U_O: -17.28 eV, β_{CC}: -2.318 eV, $\beta_{CN} = \beta_{CC}$; β_{CO}: $1.2\,\beta_{CC}$; γ_{CC}: 10.84 eV; $\gamma_{NN(aza)}$: 12.81 eV; $\gamma_{NN(amino)}$: 12.98 eV; γ_{OO}: 14.58 eV. According to Ref.[13] the DCI approximation requires a changed parametrization. Since a complete set of optimal heteroatomic parameters has not been defined so far, only the resonance integrals were altered in this paper (β_{CC}: -2.79 eV, $\beta_{CN} = \beta_{CC}$; β_{CO}: $1.2\,\beta_{CC}$).

The *PPP* molecular orbital *PPP*-MOA[14] and *PPP* configuration analysis *PPP*-CA[15] has been performed within the SCI approximation. The application of these methods have been reviewed elsewhere[16]. The "molecules-in-molecule" (MIM) method (*Longuet-Higgins-Murrell*-method) is also well described in literature. A review paper has been presented recently[17]. All singly excited states are considered in the configuration interaction of the MIM calculations. The parameters are those of the *PPP* calculations.

The molecular geometry has been derived by geometry-optimized MINDO/3 (**m**odified **i**ntermediate **n**eglect of **d**ifferential **o**verlap) and QCFF/Pi (**q**uantum **c**hemical extension of the **f**orce **f**ield method to **pi**-electronic systems) calculations. Whereas the MINDO/3 method[18] represents an all-valence electron method, in the QCFF/Pi method[19] only the π-electrons are treated explicitely. The σ-system is taken into account by means of potential functions. All singly excited configurations are considered in the configuration interaction. In calculating **4** the NMe_2 group was replaced by the NH_2 group. Whereas the NH (100 pm) and CH bond lengths (110 pm) and NH_2 bond angles 120° were kept fixed in the MINDO/3 calculation, no variables have been fixed in the QCFF/Pi calculation. The parameters employed in the MINDO/3[20] and QCFF/Pi[21] method are those contained in the standard program available by the quantum chemical program exchange (QCPE).

Results and Discussion

Results of *PPP* calculations of **4** are assembled in Table 1. The results of the calculation within the DCI approximation (*PPP*/1) differ appreciably from those within the SCI approximation (*PPP*/2), although long wavelength absorptions are predicted in both cases. The S_1 and S_3 singlet excited states of the DCI calculation consist mainly of singly excited configurations like those of the SCI calculation. The S_2 state, however, is mainly described by a twofold electron excitation from the highest occupied (HOMO) to the lowest unoccupied MO (LUMO). The better agreement between the position of the colour band of the *PPP*/1 calculation relative to that of the *PPP*/2 calculation is surely fortuitous and should not be overestimated.

Since only the singly excited configurations determine the colour band of **4** the results of the SCI are discussed and analyzed in more detail. The π-electron distribution of the ground state S_0 and the change of the

Table 2. *The two lowest MIM transition energies and oscillator strengths (in parenthesis) of 2-dimethylamino-3-azacyclopentadienone* (**4**) *calculated from differently fragmented molecules*

Fragments	Transition[a] (in µm^{-1})	Ground state depression (in eV)
5	1.34 (0.11) 3.49 (0.28)	– 0.6399
6	0.50 (0.06) 2.64 (0.29)	– 1.5233
7	0.52 (0.16) 2.13 (0.11)	– 2.1899
5[b]	1.65 (0.14) 3.68 (0.18)	– 0.3570

[a] MIM transition energy calculated with neglection of the lowering of ground state energy (cf. text). The related *PPP* transitions are: 1.36 (0.03) and 3.67 (0.53) (cf. Table 1: *PPP*/2).

[b] MIM transition energies with an additional bond parameter that is chosen according to the increased bond lengths (β_{CC} = – 1.707 eV). The related *PPP* transition energies are: 1.67 (0.04) and 3.84 (0.50) (cf. Table 1: *PPP*/3).

electron densities upon $S_0 \rightarrow S_1$ excitation are shown in Fig. 1. Although the CC resonance integrals are fixed and equalized in the calculation a remarkably low π-bond order is calculated between the atoms 1 and 2 of **4**. This finding suggests that **4** is strongly related to that open chain structure which differs from **4** in the absence of the 1–2 bond. This is the merocyanine reference structure **5**. In fact, the change of the charge densities upon $S_0 \rightarrow S_1$ excitation and the direction of the transition moments relative to the molecular framework clearly reveals the strong relationship between **4** and **5** (cf. Fig. 1).

This conclusion is supported by *PPP* configuration analysis. As shown in Fig. 2a there is an excellent correlation between the ground and excited states of **4** and **5**. The ground state Ψ_0 of **4** is described to 92% by the ground state Ψ_0^0 of the reference structure **5**. Including the small contributions from the excited states of **5** the ground state is reproduced to 99.8% (r_M-value). A good correlation is also found between the Ψ_1 state of **4** and Ψ_1^0 state of **5** (87%) while the Ψ_2 state of **4** correlates both to the Ψ_2^0 state (47%) and the Ψ_3^0 state (40%) of **5**.

Since both the excited state wavefunction Ψ_1 and Ψ_1^0 results essentially from one electron transitions from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO) the nature of these orbitals should be considered in more detail. The correlations between the frontier orbitals of **4** and **5** are part of the MO analysis. They are shown in Fig. 3. There is an excellent correlation between the HOMOs and LUMOs of both structures.

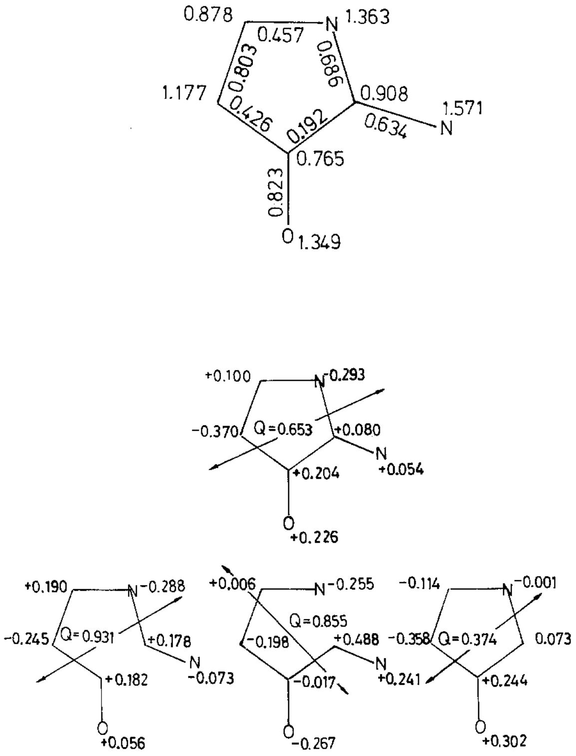

Fig. 1. Molecular diagrams (electron densities q_r and bond orders p_{rs}) of **4** in the molecular ground state and change of the electron densities upon excitation ($\Delta q_r = q_r^* - q_r$) and direction of the transition moment Q of $S_0 \rightarrow S_1$ transition of **4** and the fragmented molecules **5** to **7**

The results of the frontier orbital analysis allow one to look for an understanding of the change of spectral transition energy of **4** upon ring closure on passing from **5** to **4**.

According to the qualitative first order perturbational MO theory[22] introduction of the additional π-bond on passing from **5** to **4** (dotted line in Fig. 4) will destabilize the HOMO (negative product of the coefficients of the joint atoms) but will stabilize the LUMO (positive product of the coefficients). Consequently the energy gap between the HOMO and

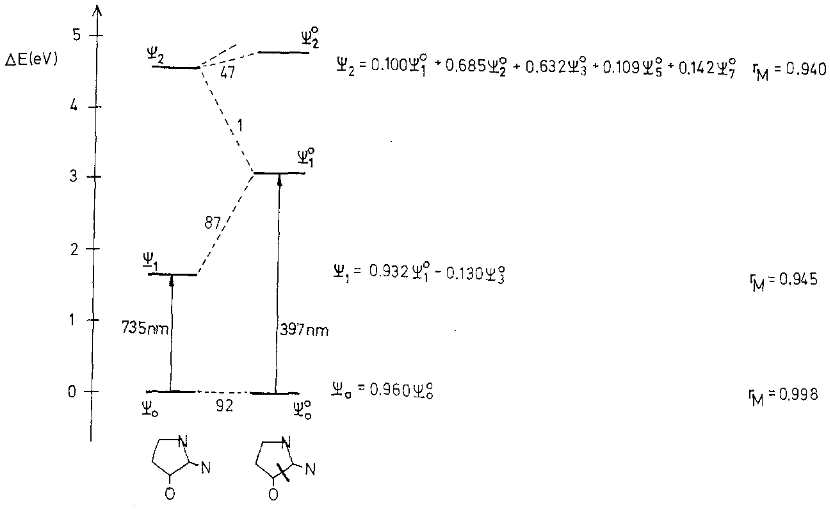

Fig. 2a

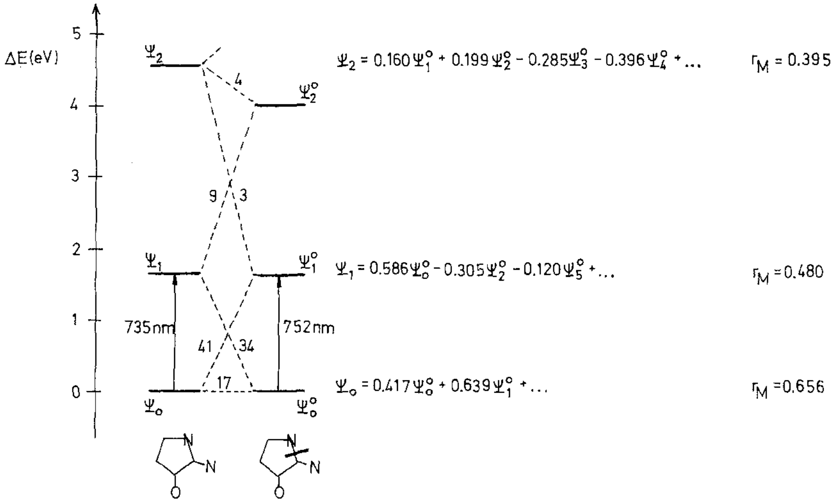

Fig. 2b

Fig. 2a–c. Correlation diagrams between the electronic states of 2-dimethylamino-3-azacyclopentadienone **4** and those reference structures **5** to **7** according to the results of *PPP*-CA calculations. States are understood as correlated and are connected by dashed lines if the contributions exceed 1%. The main contribution of the electronic states of the reference structure are given on the right side ($|c_{r\mu}| \geqslant 0.1$; Ψ_0^0, Ψ_1^0, delocalized wavefunctions; Λ_1, Λ_2, localized wavefunctions; T_1, T_2, charge transfer wavefunctions; Γ_0 no bond ground state wavefunction). Only electronic states with $\Delta E \leqq 5\,\text{eV}$ are shown in the figure. The energies of the ground states are arbitrarily set equal zero

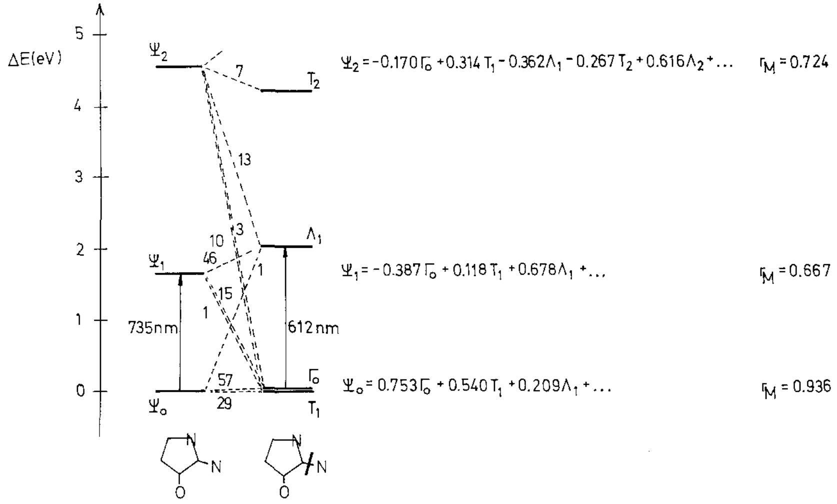

Fig. 2c

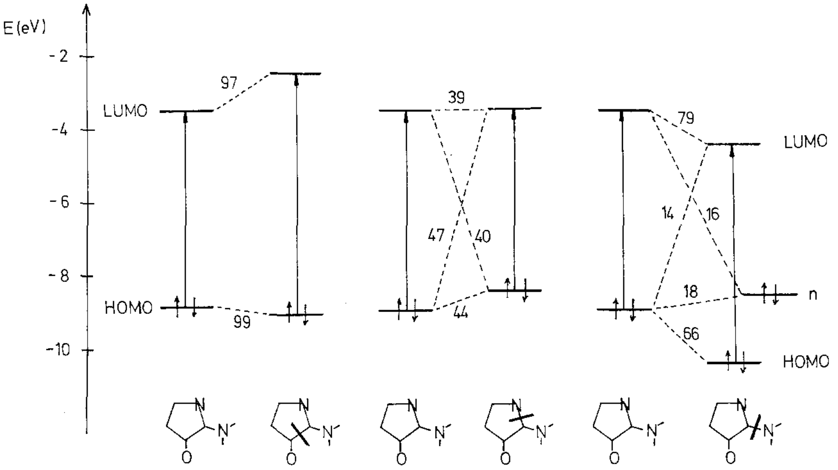

Fig. 3. Correlation diagrams between the frontier orbitals of **4** and those of the reference structures **5** to **7** according to the results of the MO analysis. The correlating states are connected by dashed lines if the contributions exceed 5%

LUMO is reduced. This is equivalent to a decrease of the excitation energy between ground state S_0 and lowest energy excited state S_1 upon ring closure.

The effect of cyclization on the electronic states of the merocyanine can be pursued quantitatively by the MIM method. Due to the neglection of doubly and higher excited configurations the ground state energy depression should not be taken into account. As shown in Table 2, the lowest MIM transition energies of **4** starting from the open chain molecule **5** are nearly those obtained by *PPP*/2 calculation. Thus based on the composite molecule approach the change in the chromophoric properties on passing from **5** to **4** is well understood qualitatively and well reproduced quantitatively.

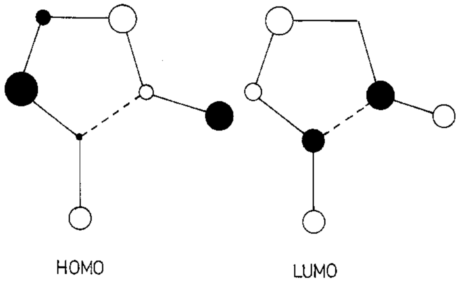

Fig. 4. Pictorial representation of the coefficients of the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) of **5**. The diameter of the circular lobe is proportional to the size of the atomic orbital coefficients

The situation is by far more complicated if we refer **4** to the acyclic structure **6** although the nearly equal $S_0 \rightarrow S_1$ transition energies of **4** and **6** may suggest a close relationship between their electronic states. According to the configuration analysis this is not the case. The correlation diagram (Fig. 2 b) shows that the correlation between the electronic states is very complex. The ground state of **4** corresponds to the first excited state of **6** rather than to its ground state. The inverse holds for the excited state of **4**. Moreover, the wavefunctions of **4** are very incompletely reproduced by those of the reference structure (low r_M-values).

Also the MO-analysis reveals appreciable mutual correlations between the HOMOs and LUMOs of **4** and **6** (Fig. 3).

In the MIM calculation, the ground state depression is relatively high (cf. Table 2) and the MIM transition energies of **4** are considerably too low. Thus the electronic states of **4** and **6** are dissimilar and the electronic transition occurring between them are of different origin. In other words, the close agreement between the longest wavelength absorption of **4** and **6** is fortuitous and **6** cannot be considered as the parent chromophore of **4**, although their wavelengths are in the same order of magnitude.

For similar reasons also azacyclopentadiene is not the proper substructure of **4**. According to the *PPP*-CA calculations of **4** with respect to **7** the effect of the NMe_2 substitution on the electronic wavefunction is relatively strong. Due to the low-energy amino-to-azacyclopentadienone charge transfer configuration T_1* the no-bond ground state Γ_0 of the fragmented structure **7** strongly mixes with the T_1 configuration (Fig. 2 c). Also the first excited state Ψ_1 of **4** is represented by a complex mixture of the no-bond ground state Γ_0, the charge transfer configuration T_1 and the locally excited configuration Λ_1 of the reference structure **7**. This result is already predetermined by the correlation of the frontier orbitals (cf. Fig. 3). The orbital of the amino group of the fragmented structure **7** is involved both in the HOMO and LUMO of **4**. Therefore, the substituent effect cannot be easily predicted by qualitative PMO theory and MIM transition energies, being in disagreement with the *PPP* transition energies due to the strong ground state depression (Table 2). Thus, the strong interaction between amino substituent and the ring renders the description of the colour of **4** unsuited in terms of the azacyclopentadienone parent chromophore.

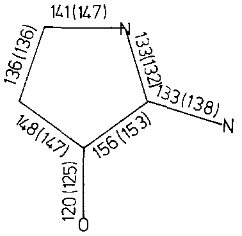

Fig. 5. Calculated bond lengths of **4** in pm obtained by the geometry-optimized MINDO/3 and QCFF/Pi calculations (in parenthesis)

The above results are essentially unchanged if the idealized structures are replaced by more realistic ones which are based on calculated molecular geometries. Both the MINDO/3 and QCFF/Pi calculation of **4** (NH_2 instead of NMe_2) predict one extremely long CC bond ($r_{CC} \geqslant 153$ pm) between the atoms 1 and 2 (Fig. 5). The results will additionally favour the reference structure **5** over the reference structures **6** and **7**. If the bond length expansion is taken into account (*PPP*/3 calculation in Table 1) the calculated absorption wavelength of

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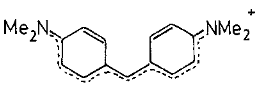
* The greek letter T refers to CT singlet configuration and should not be mixed up with the triplet configuration.

4 is similar to that found experimentally for the 4,5-diphenyl derivative (ca. 600 nm). The phenyl groups are probably rotated out of the plane because of steric hindrance and hardly affect the longest-wavelength absorption.

The geometry-optimized QCFF/Pi calculation predicts the colour band of **4** at about 500 nm (NH_2 group instead of NMe_2 group). As found for chain merocyanine dyes the absorptions are generally calculated at too low wavelengths by this method[23]. This may be due to an unsatisfactory parametrization of the heteroatoms in the QCFF/Pi calculations. This deficiency is also reflected in the large differences in the calculated lengths of the CN and CO bonds between the QCFF/Pi and MINDO/3 calculation (cf. Fig. 5).

All the results obtained reveal that the comparison of the wavefunctions provides a more proper theoretical basis in defining the basic chromophore than the comparison of the transition energies.

It can only be mentioned here that consideration of further examples has led to similar conclusions. The nearly equal absorption wavelengths of *Michler*'s Hydrol Blue (**8**) and streptononamethinecyanine (**9**, $n = 4$) suggested that the chain cyanine is the basic chromophore of **8**[8].



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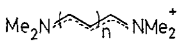

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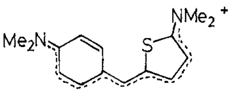
However, the relationship is more complex as anticipated, for both ground and excited state of **8** strongly involve the additional double bonds. Moreover, the assumption of a basic cyanine chromophore in diarylmethane dyes leads to completely wrong conclusions in other cases. Whereas **9** ($n = 4$) should be the basic chromophore of **10** and **11**, **9** ($n = 3$) and **9** ($n = 2$) might be considered as the basic chromophore of **12**, **13** and **14**, respectively. Although the cyanine basic chromophore differs in chain lengths, the compounds **10** to **14** absorb at nearly the same wavelengths, however[24]. The structures **10** to **14** seem to be chromophorically related to *Michler*'s Hydrol Blue (**8**) rather than to a single definite chain structure.



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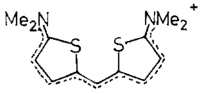

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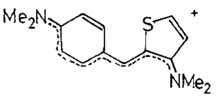

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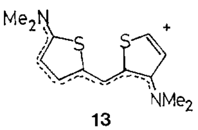
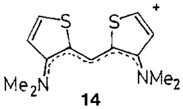


13



14

Conclusions

Our study gives rise to the following conclusions:

1. Generally, identity of the absorption wavelength of the colour band is not the proper basis of the definition of the parent chromophore. As demonstrated with **4** any coincidence in the wavelengths may just be fortuitous. This coincidence cannot be explained transparently by simple composite molecule approaches.

2. Molecular orbital and configuration analysis define the parent chromophore by the extent of electronical relatedness between the chromophores under comparison. Based on this definition **5** is the by far the more proper parent chromophore of **4** than **6** and **7**. The basic chromophore defined by this way has the great advantage that simple quantitative (molecules-in-molecule method) or qualitative treatments (perturbation molecular orbital method) can still be used to derive colour-structure relationships. However, the absorption wavelength resulting from structural modification may markedly change and can even exceed the about 100 nm found in passing from the H-indigo chromophore to indigo.

3. Although the best basic chromophore can be defined theoretically the development of colour-structure relationships may necessitate alternative reference structures. Thus, for qualitative considerations **4** can be referred to the cyclic subchromophore **7**.

4. If the position of the colour band of the basic chromophore and the chromophore is strongly shifted, it might be justified for practical reasons to consider the latter one as a new chromophoric system defining a basic chromophore itself. Along these lines **4** belongs to the cyclic chromophore of the iso-π-electronic series **15**.

15

a: $X = NR_2$, $Y = O$
b: $X = O^{-1/2}$, $Y = O^{-1/2}$
c: $X = NR_2^{+1/2}$, $Y = NR_2^{+1/2}$

An extremely long wavelength absorption has been predicted for the symmetric structure **15c** by *PPP* calculations[25]. QCFF/Pi calculations of **15** provided absorption wavelengths in the visible or infrared region (**15a**: 672 nm, **15b**: 872 nm, **15c**: 1311 nm).

Acknowledgements

We wish to thank Dr. *E. Gey* and Dr. *Th. Steiger* (Acad. Sc. DDR, Berlin) and Doz. Dr. *K. Gustav* and Dr. *J. Sühnel* (Univ. Jena) for supplying copies, respectively, of the MINDO/3 and QCFF/Pi program. We are grateful also to Prof. *O. E. Polansky* (Max-Planck-Institut für Strahlenforschung, Mülheim/Ruhr) for constructive comments on the manuscript.

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