Anti-aromaticity and Colour in Dyes Containing Unsaturated Five-membered Ring Systems

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It is shown that electronic absorption characteristics of many examples of dye molecules containing unsaturated five-membered ring systems can be explained in terms of anti-aromaticity of the rings. The criteria used to assign anti-aromatic character are specified. These are less restrictive than in the original definition of anti-aromaticity given by Breslow.

The structure and properties of some classes of organic molecules (especially typical organic dyes) which contain an unsaturated five-membered ring can be interpreted in terms of the anti-aromatic properties of the cyclopentadienyl cation (CPC) 1. Within this concept, the anti-aromatic CPC is the basic chromophore of these coloured compounds. The rationale of this interpretation is the analogy between the structure and properties of 1 and of more complex molecules whose structural features are determined by anti-aromaticity. This concept makes it possible to explain and predict the structure of relatively small coloured molecules with excitation energies of the order of \( \Delta E \) ca. 1 eV.

The term anti-aromaticity was coined by Breslow and was meant to connote and emphasize the characteristics of certain \( 4\pi \) monocytes. The most general definition was given by Breslow. A cyclic conjugated system is considered to be anti-aromatic if its \( \pi \)-electron energy is higher than that of a suitable reference compound which is not cyclically delocalized.

This energy criterion is applicable only to typical monocyclic anti-aromatic systems, e.g. cyclopentadienyl cation 1, but is not applicable to molecules with a complex geometry and topology, e.g. polycyclic systems with heteroatoms. In the case of such molecules, the choice of a suitable system for comparison is imprecise or even impossible. Even in some relatively simple cases the energy criterion is not applicable. Such an example is the simplest heterocyclic analogue of 1 with a nitrogen atom instead of a CH group in the five-membered ring, i.e. \( \text{C}_5\text{H}_3\text{N}^- \) (2) which is a typical anti-aromatic system (vide infra). Following the discussion on anti-aromaticity of 2 where the energy criterion is not applicable, we demonstrate \( \pi \)-electron energy and the energies for the open-chain reference compounds (i.e. 2a-c) calculated by the Hückel method (\( q_K = x + \beta; p_{C-\text{N}} = 0 \)) (see Table 1). Whether or not the cyclic molecule has anti-aromatic character depends on which open-chain system is used for comparison.

The two derivatives 3 and 4 of CPC are typical anti-aromatic systems corresponding to all the physical features which characterize the structure and properties of such systems. However, the \( \pi \)-electron energy calculated by the Hückel method (Table 1) of the cyclic anti-aromatic form 3 is lower than the \( \pi \)-electron energy of the open-chain streptopolymethincyanine, 3a, and therefore 3 should not have anti-aromatic character by the energy criterion. Compound 4 also has no anti-aromatic character by the energy criterion, irrespective of the open-chain systems (4a, 4b) used for comparison (energies are calculated by the HMO method).

These examples and many more show that the term 'anti-aromaticity' needs a more general definition which is independent of the open-chain system used for comparison and is also applicable to complex molecules. These criteria must be based on the physical peculiarities characteristic of the structure of anti-aromatic systems.

Typical monocyclic, homonuclear, anti-aromatic systems with \( 4n \) electrons and \( D_{oh} \) symmetry, like the cyclopropenyl anion (5), the cyclopentadienyl cation (1), the cycloheptatrienyl anion (7), and cyclobutadiene (6) are Jahn–Teller active systems. For these compounds, a significant second order Jahn–Teller effect is observed which leads to a decrease

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Table 1 \( \pi \)-Electron energies \( \Delta \) (in \( \beta \) units) of cyclic compounds with a five-membered ring and open-chain reference compounds and differences of the \( \pi \)-electron energies between the cyclic and open-chain reference compounds \( \Delta(\Delta \pi) \) (in \( \beta \) units)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta )</th>
<th>( \Delta(\Delta \pi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6.606</td>
<td>-</td>
</tr>
<tr>
<td>2a</td>
<td>6.458</td>
<td>-0.148</td>
</tr>
<tr>
<td>2b</td>
<td>6.648</td>
<td>0.042</td>
</tr>
<tr>
<td>2c</td>
<td>6.340</td>
<td>-0.266</td>
</tr>
<tr>
<td>3</td>
<td>11.061</td>
<td>-</td>
</tr>
<tr>
<td>3a</td>
<td>10.978</td>
<td>-0.084</td>
</tr>
<tr>
<td>4</td>
<td>11.091</td>
<td>-</td>
</tr>
<tr>
<td>4a</td>
<td>10.872</td>
<td>-0.619</td>
</tr>
<tr>
<td>4b</td>
<td>10.318</td>
<td>-0.773</td>
</tr>
</tbody>
</table>

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in the symmetry of the ring with an anomalous alternation of the bond distances within the ring.

Ab initio calculations show that a Jahn–Teller distortion of the CPC exists. Using ab initio calculations it was shown that the singlet–triplet energy gap is smaller than 10 kcal mol\(^{-1}\). From this small singlet–triplet energy gap it can be concluded that the ground state is a singlet state in the case of substituted CPC and of more complex molecules with a CPC fragment. This is also shown by our ab initio and semiempirical calculations for substituted CPC.

Polycarbocyclic and polyheterocyclic 4\(\pi\)-conjugated ions are also anti-aromatic systems. In the (4\(n\) + 2)\(\pi\) systems, HMO considerations differentiate between two classes of conjugated polycyclic species: systems endowed with \(C_3\) or higher axial symmetry for which the highest occupied and lowest unoccupied orbitals appear in pairs e\(\sigma\) systems with lower axial symmetry in which no such orbital degeneracies exist. In the polycycles reduced to dianions, the first class may exist. In the polycycles reduced to dianions, the first class may exist. Using HMO considerations differentiate between two classes of substituted CPC and of more complex molecules with a CPC structural element, the sum of the net charges (Q) at the atoms of the five-membered ring can be compared with Q of the CPC (1).

The energy criterion is the most important of these. Criteria 1 and 3 can be used as additional criteria for the anti-aromatic character.

Both the molecular geometry and the energy spectrum of anti-aromatic cyclopolymerines are indications of a second-order Jahn–Teller effect.

**Computational Methods**

The results of the investigations were obtained with different quantum chemical methods: with the HMO (Hückel MO) method and the PPP (Pariser, Parr, Pople) procedure in \(\pi\)-electron approximation, the semiempirical all-valence electron method MINDO/3, and by ab initio calculations. The ab initio calculations were carried out by a HONDO/S program and the PPP (Pariser, Parr, Pople) procedure in \(\pi\)-electron approximation, the semiempirical all-valence electron method MINDO/3, and by ab initio calculations. The ab initio calculations were carried out by a HONDO/S program.

There is a good qualitative agreement in the numerical data obtained by the different quantum chemical methods. Therefore, in the following sections only the results obtained with one of the above computational methods are given. Only in some cases are the results obtained with different methods given for comparison.

**Results and Discussion**

**Molecular Geometry.**—In general, there is no orbital splitting or splitting of the energy states in substituted anti-aromatic ring systems or in their heterocyclic derivatives. The geometries of these compounds correspond to relatively stable Jahn–Teller distorted structures. This is shown in Fig. 1 for the two Jahn–Teller structures 1A\(1\) and 1A\(2\) of the CPC (1). These are compared with the geometries of the amino-substituted CPC.

The similarity in the geometries of the Jahn–Teller forms of the CPC and of their substituted derivatives can be explained qualitatively by the perturbation theory in \(\pi\)-electron approximation. The degenerate bonding \(\pi\) MOs of the CPC belong to the twofold degenerate representation e\(\sigma\). One of the three symmetry planes orthogonal to the molecular plane (e.g. those which contain the y axis, see Fig. 2) is termed \(\sigma\). Then, one of the two degenerate \(\pi\) MOs is always symmetric [\(\Psi(S)\)], and the other one is anti-symmetric [\(\Psi(A)\)] in relation to \(\sigma\).

**Two** two functions are transformed to those which belong to the irreducible representations \(A_2\) and \(B_1\) if the symmetry of the rings is decreased from \(D_{5h}\) to \(C_2\), [eqn. (1)]

\[
\Psi(S) \rightarrow \Psi(A_2) = c_0\Psi_0 + c_1\Psi_4 + c_2\Psi_2 + \Psi_3
\]

\[
\Psi(A) \rightarrow \Psi(B_1) = d_1(\Psi_1 - \Psi_4) + d_2(\Psi_2 - \Psi_3)
\]

Corresponding to the perturbation theory for degenerate

\* 1 cal = 4.184 J.
orbital energy $Y(A)$ is not changed by eqn. (2), e.g., by substitution of an atom in the five-membered ring. This can be expressed by the secular determinant:

$$
\begin{vmatrix}
\langle \Psi(S)|\hat{h}|\Psi(S)\rangle - \varepsilon & \langle \Psi(S)|\hat{h}|\Psi(A)\rangle \\
\langle \Psi(S)|\hat{h}|\Psi(A)\rangle & \langle \Psi(A)|\hat{h}|\Psi(A)\rangle - \varepsilon
\end{vmatrix} = 0
$$

If a CH group within the five-membered ring is substituted by an atom X (e.g. in position 0) (see Fig. 2) then $\langle \Psi(S)|\hat{h}|\Psi(A)\rangle = 0$, and the change of the energies of the degenerate MOs is given by eqn. (2), $\varepsilon(A) = \langle \Psi(A)|\hat{h}|\Psi(A)\rangle = 0$ [that means the orbital energy $\Psi(A)$ is not changed].

$$
\varepsilon(S) = \langle \Psi(S)|\hat{h}|\Psi(S)\rangle = c_x^2\langle \Psi_x|\hat{h}|\Psi_x\rangle = 2/5h_\beta. \quad (2)
$$

The Hamiltonian perturbation is termed by $h$ and $h_\beta$. 

The calculated excitation energies are given in Table 2. These calculations include all single and some double excited configurations.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E$ (eV)</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5.17</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>4.27</td>
<td>-</td>
</tr>
<tr>
<td>8a</td>
<td>3.40</td>
<td>-</td>
</tr>
<tr>
<td>8b</td>
<td>2.89</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1.01</td>
<td>1.000</td>
</tr>
<tr>
<td>10</td>
<td>1.24</td>
<td>1.000</td>
</tr>
<tr>
<td>9a</td>
<td>1.28</td>
<td>0.518</td>
</tr>
<tr>
<td>10a</td>
<td>1.31</td>
<td>0.270</td>
</tr>
<tr>
<td>12</td>
<td>1.13</td>
<td>0.559</td>
</tr>
</tbody>
</table>

The effect of substitution in the case of anti-aromatic Jahn–Teller structures is small or opposite. The substitution of a CH atom by any substituent in the case of polyenes, if the conjugated system is extended by increasing the number of vinylene groups, is connected with a red shift of the longest-wavelength absorption (see Fig. 3). The excitation energy of the vinyl-substituted CPA i.e. anion 11, decreases by 0.9 eV in relation to the CPA itself, i.e. 8 (PPP calculation, the CI included all single and some double excited configurations). The effect of substitution in the case of anti-aromatic Jahn–Teller structures is small or opposite. The substitution of a CH atom by any substituent in the case of polyenes, if the conjugated system is extended by increasing the number of vinylene groups, is connected with a red shift of the longest-wavelength absorption (see Fig. 3). The excitation energy of the vinyl-substituted CPA i.e. anion 11, decreases by 0.9 eV in relation to the CPA itself, i.e. 8 (PPP calculation, the CI included all single and some double excited configurations).

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The energy of the longest-wavelength absorption band is decreased on the annelation of the cyclopentadienyl anions (CPA) (8, 8a, 8b) which are aromatic (4n + 2) π-electrons and by a perturbation caused by the substitution of an atom by an aromatic ring system or by annelation. The result is a decrease of the energetic distance between the HOMO and the LUMO resulting in a red shift of the longest-wavelength absorption (see Fig. 3). The perturbation of an anti-aromatic system (in our special case 1) is connected with an increase of the HOMO–LUMO gap [ΔE = $\varepsilon$(LUMO) - $\varepsilon$(HOMO)] and therefore results in a blue shift (Fig. 3).

The excitation energy for the longest-wavelength absorption band is decreased on the annelation of the cyclopentadienyl anions (CPA) (8, 8a, 8b) which are aromatic (4n + 2) π-electrons and by a perturbation caused by the substitution of an atom by any aromatic ring system (vide infra). Corresponding to the second-order perturbation theory, the change of the energy of the MO $\Psi(S)$ caused by the substitution of a CH atom by any substituent (see Fig. 2) is given by eqn. (3). The sum is formed for all the

\[\Psi(A) \quad (1)
\]

\[\varepsilon(S) = \frac{1}{2}h_\beta \quad (2)
\]
substituted aromatic CPA, 14, the excitation energy increases (blue shift), but the excitation energy decreases with increasing of the angle $\theta$ for the phenyl-substituted anti-aromatic CPC, 13. Qualitatively similar results were obtained by PPP calculations (see also Table 2).

**Electron Distribution within the Five-membered Ring of CPC Derivatives.**—The sum of the $\pi$-electron net charges within the five-membered ring of the CPC is given by eqn. (6) ($Z_0$ is the core charge of atom $\mu$). Substitution of a $\mathrm{H}$ atom by an electron donor substituent or annelation decreases $Q$ of the five-membered ring. This can be seen from Table 3. The data in Table 3 show also that there is a reversed relationship between $Q$ and $\Delta E$ [i.e., $Q = E(\text{LUMO}) - E(\text{HOMO})$] in the case of CPC, but a direct relationship between $Q$ and $\Delta E$ for the aromatic CPA. Such a reversed relationship between $Q$ and $\Delta E$ also exists in the annelated CPC which can be seen from the following data obtained by the PPP method (Table 2). The MINDO/3 optimized geometry of the benzocyclopentadienyl cation (9a) corresponds to the $^1A_0(2)$ form of the CPC. 9 The MINDO/3 optimized geometry of the fluorenyl cation (10a) is also similar to the geometry of the $^1A_1(1)$ structure of CPC. The $\pi$-electron net charges and excitation energies calculated by the PPP procedure for 10 and 10a are given in Table 2. The $\pi$-electron net charges and the total electron net charges are qualitatively similar. The $\pi$-electron net charges of the five-membered ring can be used as a qualitative criterion for the anti-aromatic character of more complex systems.

**Comparison with Experiment**

The fundamental concept that the CPC is the basic chromophore of some classes of dyes containing an unsaturated five-membered ring is demonstrated by several examples. A great number of compounds with an anti-aromatic structural element are described in a recent review. and therefore only a few examples from the review are given. Some compounds not mentioned in ref. 16 are demonstrated in this section, especially dyes with an anti-aromatic CPC chromophore.

**Amino Derivatives of CPC.**—The simplest known derivatives of CPC, i.e., 15a–c have recently been synthesized by Gompper and Glöckner. The energy of the longest-wavelength $\pi,\pi^*$ transition of 15a and 15b is 1.69 eV and 1.99 eV (in Ac$_2$O), respectively. The calculated excitation energies (using PPP standard parameters) are (in brackets are the oscillator strengths): $\Delta E (15a) = 1.44$ eV (0.032), and $\Delta E (15b) = 1.86$ eV (0.005). Further examples for relatively small molecules with an anti-aromatic CPC element which absorb at long wavelengths are compound 16, and aza- and diaza-analogues of CPC, i.e., 17, 18, and 19.

1,3-Diamino derivatives of the CPC are not known, but the benzo-condensed derivative 20 has formerly been investigated without an explanation for the unusually small excitation energy ($\Delta E = 2.71$ eV, calculated value (PPP) $\Delta E = 2.83$ eV). The excitation energy of the longest-wavelength absorption of the corresponding streptocyanine 21 is 4.34 eV.

The dimethylamino-substituted pentaphenylcyclopentadienyl cations with longest-wavelength absorptions between 500 and 800 nm are described in an earlier paper. These compounds are stable only below $-50^\circ$C. An experiment to synthesize a tetradimethylamino)cyclopentadienone is mentioned by Breslow.
In the case of 1,3-dimethylamino-substituted pentalene (22) and azapentalene (23), the anti-aromatic structure is probably stabilized by the aromatic CPA fragment. Both compounds 22 and 23 are characterized by an extremely long-wavelength absorption.

The compounds 24 and 24a are examples of cyclophycocyanines. The longest-wavelength absorption (both compounds are blue coloured) can be explained by an anti-aromatic CPC chromophore. The structures 25 and 26, so far unknown, correspond to Jahn–Teller forms of the CPC.

The MINDO/3 optimized structures express the geometry criterion of the anti-aromatic character of these structures. The benzo-condensed structures, the enolate anions of the 1,2- and 1,3-indanedione 27 and 28, have been described. As in the case of structures 25 and 26, the MINDO/3 optimized geometries are characterized by an anomalous bond alternation which is a typical feature of the anti-aromatic character of the five-membered rings in the structures (side supra). The sum of the $\pi$-electron net charges within the five-membered rings has a positive value calculated by different quantum chemical procedures. The calculated excitation energies of the structures 25 to 28 are given in Table 4.

The alkaline solutions of 27 (in alcohol) are blue, those of 28 are red. The instability of the 1,2-indanedione enolate anion 27 is probably caused by a strong electronic-vibronic interaction. The blue shift effect of a benzo condensation, typical of anti-aromatic systems, can also be observed in the case of compounds 25 and 26 compared to the structures 27 and 28, respectively. Former NMR investigations were interpreted in terms of the formation of anti-aromatic system 29 rather than 30.

Ficken and Kendall observed a red shift of the longest-wavelength absorption of compound 31 ($\lambda_{\text{max}} = 652.5$ nm) relative to 32 ($\lambda_{\text{max}} = 755$ nm). This red shift is caused by the anti-aromatic character of the five-membered ring in structure 32, in line with the localization of a positive net charge ($Q = 0.416$, calculated with the PPP method using standard geometry) of the five-membered ring.

Anti-aromatic Derivatives of Diphenylmethane and Triphenylmethane Dyes—Anti-aromatic structures were not taken into account in the investigations of the structures and properties of substituted fluorones by Brown and Dewar. Barker and Barker observed a strong red shift effect in the cyclization of

* Based on the $^1$H chemical shifts of the short-lived blue cation.
triphenylmethane dyes to fluorene derivatives. Such a red shift effect is observed, for example, for the fluorene analogues of crystal violet, 34, ($\lambda_{\text{max}} = 850 \text{ nm}$) vs. crystal violet 33 ($\lambda_{\text{max}} = 591 \text{ nm}$).46-47 The effect of the torsion of the phenyl group has no influence on the energy of the $\pi,\pi^*$ electron transition. The conjugation of the $\pi$-electron system is improved in the planar structure in relation to the twisted structure. The twisting of the phenyl group in 34 is connected with a red shift effect as expected for anti-aromatic systems. This conclusion was drawn from the results of HMO calculation^, but an explanation could not be given for the extreme red shift of structure 34 in relation to compound 33. The results of PPP calculations using standard parameters and geometries31 are given in the molecular diagram in Fig. 4 for compound 34. From the bond orders and the localization of the $\pi$ net charges within the five-membered ring of 34 it follows that this compound is a derivative of the anti-aromatic phenyl-substituted fluorenyl cation 35. Therefore, the electronic structure of 34 is better described by 34a. The sum of the $\pi$ net charges of the five-membered ring of the fluorenyl cation is $Q = 0.270$, and in the case of the phenyl-substituted fluorenyl cation with a twisted phenyl residue (\(\theta = 45^\circ\)) it is $Q = 0.226$ (PPP calculations). The sum of the $\pi$ net charges of the five-membered ring in 34 (\(Q = 0.130\)) is smaller related to compound 35 because of the presence of an electron donor (X = NMe$_2$). From Table 5 it can be seen that an increase of the torsional angle $\theta$ is followed by a red shift. If $\theta = 90^\circ$ and the coulombic interaction between the phenyl group and the fluorenyl residue in 34 is not taken into account, it can be concluded that 37 is an anti-aromatic derivative of Michler's Blue, 36. The anti-aromatic character of 37 is more significant than that of structure 34. This is also expressed by the greater value of $Q$ (0.167) in 37. Therefore, a more significant red shift absorption should be expressed for 37 in relation to 34. This qualitative prediction is confirmed by the results of PPP calculations. The calculated electron excitation energy of 37 is $\Delta E = 1.43 \text{ eV}$ (\(\lambda_{\text{max}} = 565 \text{ nm}\)), oscillator strength $f = 0.110$. The experimental value of the longest-wavelength absorption of Michler’s Blue 36 is 2.04 eV (607.5 nm), the calculated value is 2.12 eV. The significant red shift (258 nm) of 37 in relation to 36 corresponds to the change of the

### Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E_{\text{exp}}$</th>
<th>$\Delta E_{\text{PPP, CI-S}}$</th>
<th>$\Delta E_{\text{PPP, CI-S + D}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-</td>
<td>1.02</td>
<td>0.32</td>
</tr>
<tr>
<td>26</td>
<td>-</td>
<td>2.06</td>
<td>2.16</td>
</tr>
<tr>
<td>27</td>
<td>-</td>
<td>1.12</td>
<td>1.58</td>
</tr>
<tr>
<td>28</td>
<td>2.95</td>
<td>2.81</td>
<td>2.89</td>
</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>$\theta = 0^\circ$</th>
<th>$\theta = 45^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{exp}}$</td>
<td>$\Delta E_{\text{calc}}$</td>
</tr>
<tr>
<td>1.46</td>
<td>1.67</td>
</tr>
<tr>
<td>1.92</td>
<td>2.36</td>
</tr>
<tr>
<td>2.64</td>
<td>2.72</td>
</tr>
</tbody>
</table>
Table 6 Absorption maxima (nm) and sums of the n-electron net charges (HMO results) within the five-membered rings of indigoid dyes

<table>
<thead>
<tr>
<th>X</th>
<th>( \lambda_{\text{max}} )</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
<td>615</td>
<td>0.577</td>
</tr>
<tr>
<td>S</td>
<td>554</td>
<td>0.561</td>
</tr>
</tbody>
</table>

chromophoric system of Michler’s Blue (36) to an anti-aromatic structure in 37.

The protonated fluorenone imines 38a can be formulated as structures with an anti-aromatic CPC chromophore,\(^6\) The imines of fluorenone 38 are normally yellow,\(^5,10,51\) and protonation with concentrated acids results in the formation of red compounds (red shift). Contrary to this, the protonation of other imines shows a blue shift.\(^52\) The reason for the red shift on protonation of the fluorenone imines is the formation of an anti-aromatic chromophoric system.\(^49\) The MINDO/3 optimized geometry of 38a (R = H) shows a significant alteration of the bond lengths and a sum of the \( \pi \) net charges \( Q = 0.068 \) (PPP result) of the five-membered ring.

The CPC Fragment as the Chromophore of Indigo.—The absorption spectra and colour of the indigoid dyes have been explained by two different fundamental chromophore concepts. According to Klessinger and Lütke,\(^53\)–\(^55\) the so-called H chromophore 40 is the basic chromophore of indigo (39). Structure 40 absorbs at shorter wavelengths, by 118 nm, than 39. Within the polyethine concept of Dahne,\(^56\),\(^57\) the indigo chromophore is a quadrupole merocyanine which is formed by two symmetrically coupled merocyanine chains. Both chromophore concepts explain correctly many properties of indigoid dyes. A particular peculiarity of indigoid dyes, the blue shift on increasing the conjugated system, cannot be explained as well with the H chromophore as with the quadrupole merocyanine chromophore,\(^59\) i.e. 41, 42. These unusual spectroscopic shifts can be explained by two coupled anti-aromatic CPCaza analogues, e.g. 43a, as the basic chromophore of indigoids.\(^60\) The experimentally determined molecular geometry\(^60\) and the MINDO/3 optimized structure show a significant alternation of the bond lengths in agreement with one of the criteria for anti-aromatic character. The most suspicious feature of the

Aromatic CPC chromophore is the blue shift caused with the increase of the conjugated \( \pi \)-electron system (41) and (42) which cannot be explained either by the H chromophore or by the quadrupole merocyanine chromophore (see 44 and 45 in contrast to 46 and 47). The sum of the \( \pi \) net charges within the five-membered rings are also in agreement with an anti-aromatic character of the indigo chromophore (see Table 6).

Acknowledgements

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