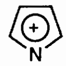
Anti-aromaticity and Colour in Dyes Containing Unsaturated Five-membered Ring Systems

Fritz Dietz,[a] **Nikolai Tyutyulkov**[a,†] **and Mordecai Rabinovitz**[b]
[a] *Universität Leipzig, Fachbereich Chemie, Leipzig, Germany*
[b] *The Hebrew University of Jerusalem, Department of Organic Chemistry, Jerusalem, Israel*

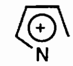
It is shown that electronic absorption characteristics of many examples of dye molecules containing unsaturated five-membered ring systems can be explained in terms of anti-aromaticity of the rings. The criteria used to assign anti-aromatic character are specified. These are less restrictive than in 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 ΔE *ca.* 1 eV.

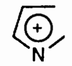

1



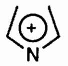
2



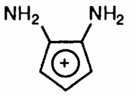
2a



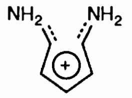
2b



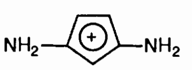
2c



3



3a



4


4a

4b


5


6


7

The term anti-aromaticity was coined by Breslow[1] and was meant to connote and emphasize the characteristics of certain $4n\pi$ monocycles. The most general definition was given by Breslow.[1] 'A cyclic conjugated system is considered to be anti-aromatic if its π-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.* $C_4H_4N^+$ (**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 its π-electron energy and the energies for the open-chain reference compounds (*i.e.* **2a–c**) calculated by the Hückel method ($\alpha_N = \alpha + \beta$; $\beta_{CN} = \beta$) (see Table 1). Whether or not the cyclic molecule has anti-aromatic character depends on which open-chain system is used for comparison.

Table 1 π-Electron energies ΔE (in β units) of cyclic compounds with a five-membered ring and open-chain reference compounds and differences of the π-electron energies between the cyclic and open-chain reference compounds $\Delta(\Delta E)$ (in β units)

Compound	ΔE	$\Delta(\Delta E)$
2	6.606	—
2a	6.458	−0.148
2b	6.648	0.042
2c	6.340	−0.266
3	11.061	—
3a	10.978	−0.084
4	11.091	—
4a	10.472	−0.619
4b	10.318	−0.773

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.[2,3] However, the π-electron energy calculated by the Hückel method (Table 1) of the cyclic anti-aromatic form **3** is lower than the π-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 $4n\pi$ electrons and D_{nh} symmetry, like the cyclopropenyl anion (**5**),[1,4–6] the cyclopentadienyl cation (**1**),[7–13] the cycloheptatrienyl anion (**7**),[14] and cyclobutadiene (**6**)[15–17] are Jahn–Teller active systems. For these compounds, a significant second order Jahn–Teller effect[8] is observed which leads to a decrease

---

† *Permanent Address:* Bulgarian Academy of Sciences, Institute of Organic Chemistry, BG-1040 Sofia, Bulgaria.

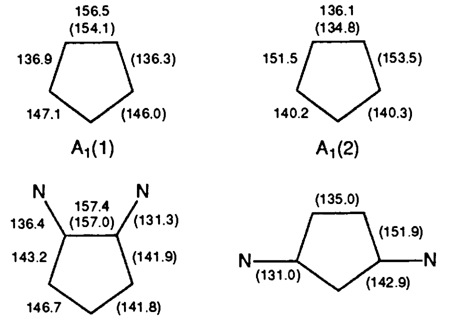


Fig. 1 Comparison of the Jahn–Teller structures of the CPC (**1**) (values in pm; calculated by *ab initio*[7] and, in brackets, MINDO/3,[2,11] respectively) and the 1,2- and 1,3-diamino-substituted derivatives[12]

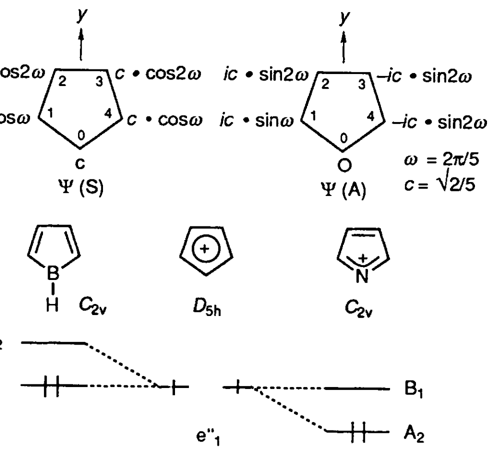


Fig. 2 Relative position of the bonding π MOs $\Psi(B_1)$ and $\Psi(A_2)$ which are formed from the degenerate π MOs e''_1 of the CPC (D_{5h} symmetry) by perturbation on substitution of a CH group by a more electronegative atom (N) and a more electropositive atom (B) than the carbon atom

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

Ab initio calculations[7–10] show that a Jahn–Teller distortion of the CPC exists. Using *ab initio*-CI investigations[8] 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[3] for substituted CPC.

Polycarbocyclic and polyheterocyclic $4n\pi$-conjugated ions are also anti-aromatic systems.[18a–f] In the $(4n + 2)\pi$ 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 *vs.* systems with lower axial symmetry in which no such orbital degeneracies exist. In the polycycles reduced to dianions, the first class may form a triplet ground state while in the second class the singlet state of the dianion is lower in energy than the triplet state. As a result the HOMO–LUMO energy gap (ΔE) of doubly charged benzenoid polycycles with $4n\pi$ systems in the path of conjugation is much smaller than in the monocyclic $4n\pi$ systems and even more so than that of the neutral $(4n + 2)$ π-electron aromatic hydrocarbons. The HOMO–LUMO gap was proposed as the criterion for anti-aromaticity of these compounds.[18g]

The logical conclusion from the literature[5–18g] is that the following fundamental criteria for an anti-aromatic character must be valid.

1. *Geometry criterion.* The geometric configurations of anti-aromatic structures are characterized by an alternation of the bond distances and anomalous long bond distances R (in typical cases $R > 150$ pm).
2. *Energy criterion.* The relatively stable Jahn–Teller forms of anti-aromatic systems have small excitation energies (*vide infra*). If the anti-aromatic $4n\pi$-electron system is perturbed the HOMO–LUMO gap is increased and a blue shift of the longest-wavelength absorption results, in contrast to aromatic $(4n + 2)$ π-electron systems where a red shift is observed. The perturbation may be caused either by a substitution of a H atom or by annelation which leads to an extension of the conjugated π-electron system.
3. *Charge criterion.* For complex anti-aromatic systems 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 cyclopolymethines 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 π-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/5 program system,[19–21] using a MINI-3 basis set.[22] 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 $^1A_1(1)$ and $^1A_1(2)$ 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 π-electron approximation. The degenerate bonding π MOs of the CPC belong to the twofold degenerate representation e''_1. One of the three symmetry planes orthogonal to the molecular plane (*e.g.* those which contain the y axis, see Fig. 2) is termed σ_v. Then, one of the two degenerate π MOs is always symmetric [$\Psi(S)$], and the other one is anti-symmetric [$\Psi(A)$] in relation to σ_v.[23,24] These 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_{2v} [eqn. (1)]

$$\begin{aligned} \Psi(S) &\longrightarrow \Psi(A_2) = c_0\Psi_0 + c_1(\Psi_1 + \Psi_4) + c_2(\Psi_2 + \Psi_3) \\ \Psi(A) &\longrightarrow \Psi(B_1) = d_1(\Psi_1 - \Psi_4) + d_2(\Psi_2 - \Psi_3) \end{aligned} \quad (1)$$

Corresponding to the perturbation theory for degenerate

---

* 1 cal = 4.184 J.

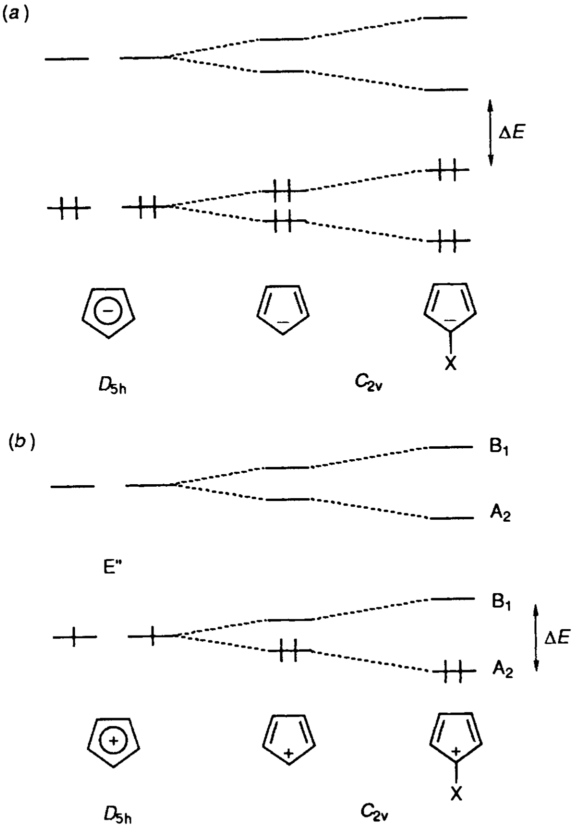


Fig. 3 Spectral shift resulting from a perturbation by increasing the conjugated π-electron system in the case of aromatic (*a*) and anti-aromatic (*b*) compounds

Table 2 Excitation energies Δ*E* (in eV) and sums of the π-electron net charges *Q* of CPA (**8**), CPC (**9**, **10**), of the vinyl-substituted derivatives and of the annelated compounds

Compound	Δ*E*	*Q*
8	5.17	—
11	4.27	—
8a	3.40	—
8b	2.89	—
9	1.01	1.000
10	1.24	1.000
9a	1.28	0.518
10a	1.31	0.270
12	1.13	0.559

states, the change of the energy ε of the degenerate states e''_1 at a perturbation *h* is determined by a change of the geometry (*e.g.* by the substitution of a CH group within the five-membered ring). This can be expressed by the secular determinant:

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

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

$$\varepsilon(S) = \langle\Psi(S)|h|\Psi(S)\rangle = c_o^2\langle\Psi_o|h|\Psi_o\rangle = 2/5h_x\beta, \quad (2)$$

The Hamiltonian perturbation is termed by *h*, and $h_x\beta$ ($\beta < 0$) is the change of the Coulomb integral of an atom X in relation to the CH group ($\alpha = \alpha_c + h_x\beta$). If the atom X is more electronegative than the carbon atom (e.g. the N atom) then $h_x > 0$ but $h_x\beta < 0$. Therefore, the energy of the orbital Ψ(S) is decreased and the occupied orbital belongs to the symmetry A_2 (see Fig. 2). From the equation of this MO it follows that the bond orders are $p_{23} > p_{12}$ for this electronic configuration. This corresponds to a geometry like form $^1A_1(2)$ (see Fig. 1).

When X is a more electropositive atom than C (*e.g.* B) $h_x < 0$ but $h_x\beta > 0$. This means that the energy of Ψ(S) is increased, and the highest occupied MO belongs to the symmetry B_1 (Fig. 2). This electronic configuration is characterized by bond orders $p_{12} > p_{23}$ and the geometry corresponds to the form $^1A_1(1)$.

From the correlation diagrams in Fig. 2 it follows that there is a correlation between the degenerate MOs belonging to the representations A_2 and B_1. These correlations are independent of whether they are a consequence of a second-order Jahn–Teller effect or whether they result from a decrease of the symmetry by substitution of a CH group by an atom X (or substitution of a H atom of a CH group).

Influence of a Perturbation on the Energy Spectrum of CPC.—The most important criterion for the distinction between aromatic and anti-aromatic systems is the change of the energy spectrum by a perturbation. This general feature can also be applied to more complex systems.

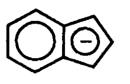
The conjugated system of aromatic monocyclic compounds with (4*n* + 2) π-electrons is increased by a perturbation caused by the substitution of a H atom by another aromatic ring system or by annelation. The result is a decrease of the energetic distance between the HOMO and the LUMO resulting in a red 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 [Δ*E* = *E*(LUMO) − *E*(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 (4*n* + 2) π-electron systems[25] (see Table 2). Contrary to this fact, there is an increase in the excitation energy of the longest-wavelength absorption upon annelation of the anti-aromatic CPC, *i.e.* **9**, **9a**, **10**, **10a** (Table2).

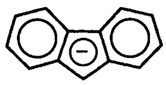
The energy of the longest-wavelength absorption also decreases in the case of polyenes if the conjugated system is extended by increasing the number of vinylene groups. This vinylogy effect is connected with a red shift of the longest-wavelength electron transition. This is expressed by the rule of König,[26] Brooker,[27] Lewis and Calvin,[28] and Platt[29] that an elongation of the conjugated chain of a polymethine $X\cdots(CH{=}CH)_n\cdots CH\cdots X$ by one vinylene group results in a red shift of about 100 nm. 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 H atom by a vinyl group within the $^1A_1(1)$ form of the CPC, *i.e.* **12**, leads to a decrease of the excitation energy of only 0.11 eV (PPP calculations including single and double excited configurations) (see Table 2). The calculated excitation energies are in a reversed relationship to the sum of the π-electron net charges *Q* of the five-membered rings (*vide infra*). Corresponding to the second-order perturbation theory, the change of the energy of the MO Ψ(S) caused by the substitution of a H atom by any substituent (see Fig. 2) is given by eqn. (3). The sum is formed for all the

8



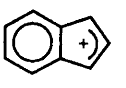
8a



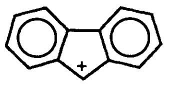
8b

9

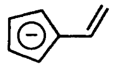
10



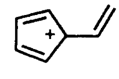
9a



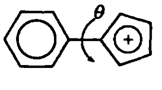
10a



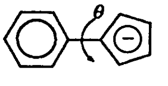
11



12



13



14

Table 3 Dependence of the sum of the π-electron net charges Q within the five-membered ring, the energy of the longest-wavelength absorption ΔE (in β units) and the total π-electron energy ε (in β units) on the torsional angle θ of the phenyl group of **13** and **14** (HMO results)

	13			**14**		
θ/°	Q	ΔE	ε	Q	ΔE	ε
0	0.403	0.164	13.966	−0.917	1.385	14.872
15	0.418	0.157	13.924	−0.922	1.385	14.846
30	0.465	0.136	13.811	−0.936	1.418	14.775
45	0.554	0.102	13.644	−0.957	1.470	14.676
60	0.699	0.059	13.457	−0.978	1.534	14.575
75	0.833	0.018	13.300	−0.994	1.593	14.500
90	1.000	0.000	13.236	−1.000	1.618	14.472

$$E_s^{(2)} = \beta_o^2 \sum_k \frac{c_{kr}^2 \cos^2 \theta}{E_s - E_k} \qquad (3)$$

bonding MOs of the substituent with the index k, β is the resonance integral of the bond between the C atoms of the CPC and the substituent, and c_{kr} is the MO coefficient of the atom r which is connected with the CPC. If the substituent is an alternant aromatic hydrocarbon then eqn. (3) has the form eqn. (4). If the MO energies E_k of the substituent are given by eqn. (5)

$$E_s^{(2)} = 2\beta_o E_s \sum_k \frac{c_{kr}^2 \cos^2 \theta}{E_s^2 - E_k^2} \qquad (4)$$

$$|E_k| > |E_s| \qquad (5)$$

then it follows from eqn. (4) that $E_s^{(2)} > 0$. In this case the HOMO belongs to the B_1 state, and the LUMO belongs to the A_2 state. This condition is fulfilled *e.g.* for the vinyl group and the phenyl group as substituents. But $E < 0$ if one or more MOs of the substituent do not fulfill eqn. (5).

The influence of a perturbation on the energy spectrum of aromatic and anti-aromatic systems can also be seen in **13** and **14**. The results of the π,π^* electron excitation energies and of the total π-electron energies of the phenyl-substituted anti-aromatic CPC **13**, and the aromatic anion (CPA), **14**, depending on the torsion angle θ of the phenyl group are shown in Table 3. These results were obtained by the HMO method. The dependence of the resonance integral on the torsional angle θ was obtained from the equation $\beta = \beta_o \cos \theta$. From Table 3 it can be seen that the absolute values of the total π-electron energies decrease with a decrease of the conjugation by an increase of the torsional angle θ for both compounds **13** and **14**. In the case of the phenyl-substituted aromatic CPA, **14**, the excitation energy increases (blue shift), but the excitation energy decreases with increasing of the angle θ 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 π-electron net charges within the five-membered ring of the CPC is given by eqn. (6) (Z_μ is the

$$Q = \sum_{\mu}^{5} (Z_\mu - q_\mu) = \sum_{\mu}^{5} (1 - q_\mu) = 1 \qquad (6)$$

core charge of atom μ). Substitution of a 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 ΔE [$= E$(LUMO) $- E$(HOMO)] in the case of CPC, but a direct relationship between Q and ΔE for the aromatic CPA. Such a reversed relationship between Q and ΔE 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 $^1A_1(2)$ 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 π-electron net charges and excitation energies calculated by the PPP procedure for **10** and **10a** are given in Table 2. The π-electron net charges and the total electron net charges are qualitatively similar. The π-electron net charges of the five-membered ring can be used as a qualitative criterion for the anti-aromatic character of more complex systems.

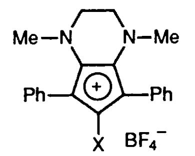
Comparison with Experiment

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[16] and therefore only a few examples from the review[16] are given. Some compounds not mentioned in ref. 16 are demonstrated in this section, especially dyes with an anti-aromatic CPC chromophore.

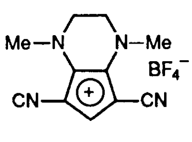
Amino Derivatives of CPC.—The simplest known derivatives of CPC, *i.e.* **15a–c** have recently been synthesized by Gompper and Glöckner.[30] The energy of the longest-wavelength π,π^* transition of **15a** and **15b** is 1.69 eV and 1.99 eV (in Ac_2O), respectively. The calculated excitation energies (using PPP standard parameters[31]) are (in brackets are the oscillator strengths): ΔE(**15a**) = 1.44 eV (0.032), and ΔE(**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**,[32] and aza- and diaza-analogues of CPC, *i.e.* **17**, **18** and **19**.[16,33–36]

1,3-Diamino derivatives of the CPC are not known, but the benzo-condensed derivative **20** has formerly been investigated[27] without an explanation for the unusually small excitation energy [ΔE = 2.71 eV, calculated value (PPP) ΔE = 2.83 eV]. The excitation energy of the longest-wavelength absorption of the corresponding streptocyanine **21** is 4.34 eV.[38]

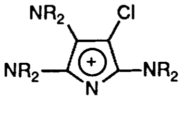
The dimethylamino-substituted pentaphenylcyclopentadienyl cations with longest-wavelength absorptions between 500 and 800 nm are described in an earlier paper.[39] These compounds are stable only below −50 °C. An experiment to synthesize a tetra(dimethylamino)cyclopentadienone is mentioned by Breslow.[40]



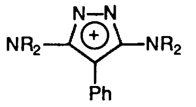
15a: X = OEt
b: X = NMe$_2$
c: X = C$_4$H$_8$N



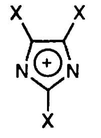
16 (green)



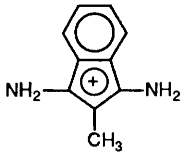
17 (red)



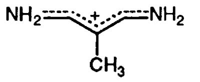
18 (blue)



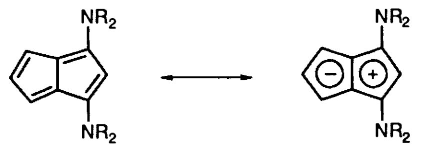
19 X = NR$_2$(yellow)
X = SR(blue)



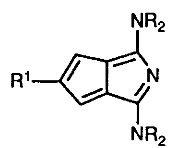
20



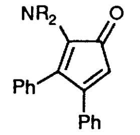
21



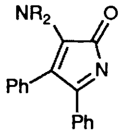
22 **22a**



23



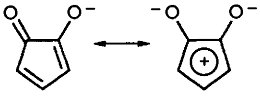
24



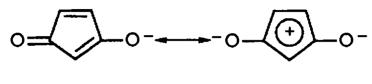
24a

In the case of 1,3-dimethylamino-substituted pentalene (**22**) and azapentalene (**23**)[41] 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.

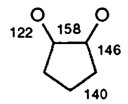
The compounds **24** and **24a**[42,43] are examples of cyclomerocyanines. The longest-wavelength absorption (both compounds are blue coloured) can be explained by an anti-aromatic CPC chromophore. The structures **25** and **26**, so far unknown, correspond to Jahn–Teller forms of the CPC.[44] The MINDO/3 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[44] 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 (*vide supra*). The sum of the π-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.[44] The alkaline solutions of **27** (in alcohol) are blue, those of **28**



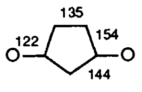
25 **25a**



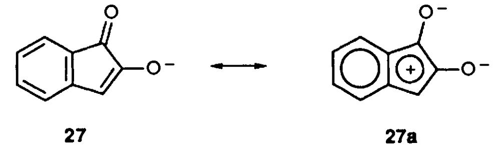
26 **26a**



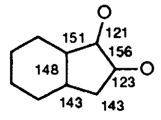
25



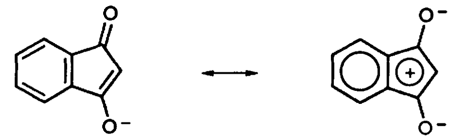
26



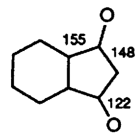
27 **27a**



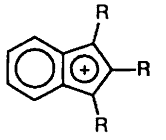
27



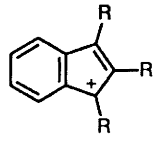
28 **28a**



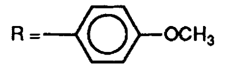
28



29



30



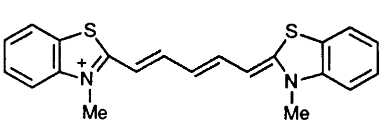
are red. The instability of the 1,2-indanedione enolate anion **27** is probably caused by a strong electronic–vibronic interaction. The blue shift effect of a benzo condensation, typical of anti-aromatic systems, can also be observed in the case of compounds **25** and **26** compared to the structures **27** and **28**, respectively. Former NMR investigations were interpreted in terms of the formation of anti-aromatic system **29** rather than **30**.[13,*]

Ficken and Kendall[45] observed a red shift of the longest-wavelength absorption of compound **31** (λ_{max} = 652.5 nm) relative to **32** (λ_{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.

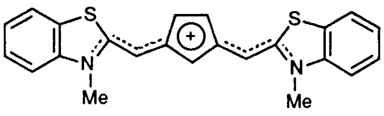
Anti-aromatic Derivatives of Diphenylmethane and Triphenylmethane Dyes.—Anti-aromatic structures were not taken into account in the investigations of the structures and properties of substituted fluorenes by Brown and Dewar.[46] Barker and Barker[47] observed a strong red shift effect in the cyclization of

---

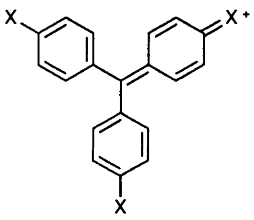
* Based on the ^{1}H chemical shifts of the short-lived blue cation.



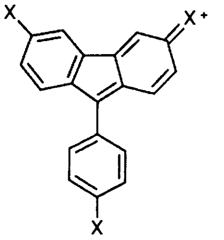
31



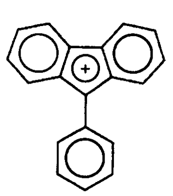
32



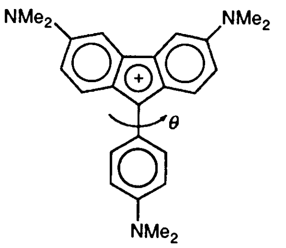
33: X = NMe_2



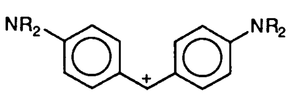
34: X = NMe_2



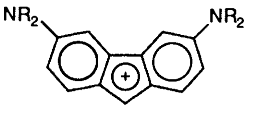
35



34a

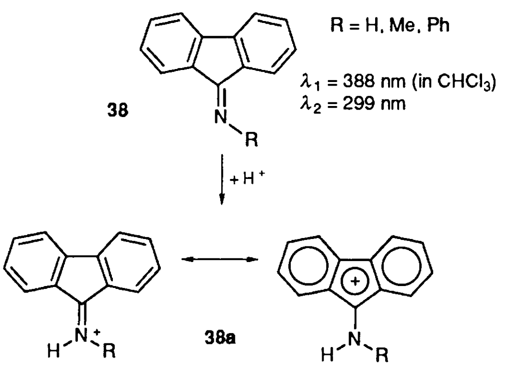


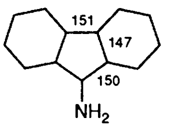
36



37

triphenylmethane dyes to fluorene derivatives. Such a red shift effect is observed, for example, for the fluorene analogues of crystal violet, **34**, (λ_{max} = 850 nm) *vs.* crystal violet **33** (λ_{max} = 591 nm).[46,47] The effect of the torsion of the phenyl group has no influence on the energy of the π,π^* electron transition. The conjugation of the π-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 calculations,[46] 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 geometries[31] are given in the molecular diagram in Fig. 4 for compound **34**. From the bond orders and the localization of the π net charges within the five-membered ring of **34** it follows that this compound is a derivative of the anti-aromatic phenyl-substituted fluorene cation **35**. Therefore, the electronic structure of **34** is better described by **34a**. The sum of the π 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 ($\theta = 45°$) it is $Q = 0.226$ (PPP calculations). The sum of the π 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 θ is followed by a red shift. If $\theta = 90°$ 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 ΔE = 1.43 eV (λ_{max} = 865 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),[48] 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





38a: R = H

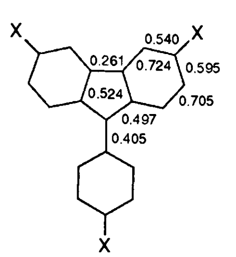


Fig. 4 Bond orders of **34**

Table 4 Electron excitation energies (PPP) ΔE (in eV) of structures **25**–**28**

Compound	ΔE_{exp}	ΔE(PPP, CI-S)	ΔE(PPP, CI-S + D)
25	—	1.02	0.32
26	—	2.06	2.16
27	—	1.12	1.58
28	2.95	2.81	2.89

Table 5 Dependence of the experimental[47] and calculated (PPP) electron excitation energies ΔE (eV) and intensities (molar extinction coefficient ε and oscillator strength f) on the torsional angle θ of compound **34a** (X = NMe_2)

		$\theta = 0°$		$\theta = 45°$	
ΔE_{exp}	$\varepsilon/10^4$	ΔE_{calc}	f	ΔE_{calc}	f
1.46	1.7	1.67	0.09	1.59	0.10
1.92	7.5	2.36	1.22	2.15	0.87
2.64	0.6	2.72	0.40	2.67	0.45

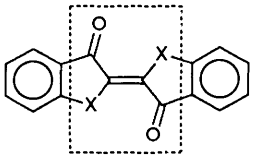
Table 6 Absorption maxima (in nm) and sums of the π-electron net charges (HMO results) within the five-membered rings of indigoid dyes **39**

X	λ_{max}	Q
NH	615	0.577
S	554	0.561

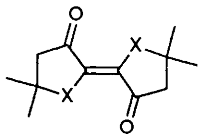
chromophoric system of Michler's Blue (**36**) to an anti-aromatic structure in **37**.

The protonated fluorenone imines **38a** can be formulated as structures with an anti-aromatic CPC chromophore.[49] The imines of fluorenone **38** are normally yellow,[50,51] 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 π net charges $Q = 0.068$ (PPP result) of the five-membered ring.

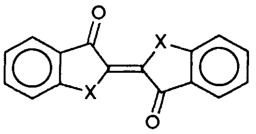
The CPC Fragment as the Chromophore of Indigo.—The absorption spectra and colour of the indigoid dyes have been explained by two different fundamental chromophore concepts. According to Klessinger and Lüttke,[53–55] the so-called H chromophore **40** is the basic chromophore of indigo (**39**). Structure **40** absorbs at shorter wavelengths, by 118 nm, than **39**. Within the polymethine concept of Dähne,[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,[58] *i.e.* **41**, **42**. These unusual spectroscopic shifts can be explained by two coupled anti-aromatic CPC aza analogues, *e.g.* **43a**, as the basic chromophore of indigoids.[59] 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 anti-aromatic CPC chromophore is the blue shift caused with the increase of the conjugated π-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 π net charges within the five-membered rings are also in agreement with an anti-aromatic character of the indigo chromophore (see Table 6).



39

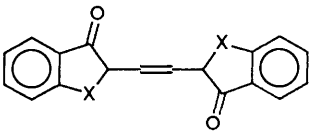


40



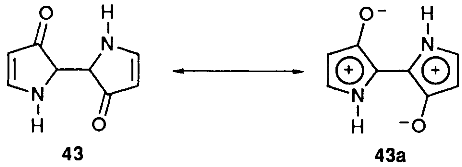
41

X = NH: λ_{max} = 615 nm
X = S: λ_{max} = 554 nm



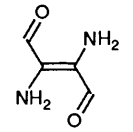
42

λ_{max} = 573 nm
λ_{max} = 534 nm



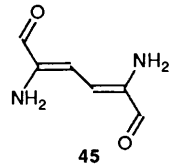
43 **43a**

experimental **43a** calculated



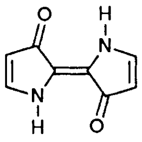
44

ΔE = 3.18 eV (f = 0.376)



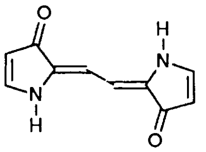
45

ΔE = 2.98 eV (f = 0.821):red shift



46

ΔE = 2.67 eV (f = 0.227)



47

ΔE = 3.16 eV (f = 0.957):blue shift

Acknowledgements

One of the authors (F. D.) wishes to thank the *Fonds der Chemischen Industrie* for financial support. N. T. as a winner of a Humboldt Research Award acknowledges support of the Alexander von Humboldt-Stiftung.

References

1 (*a*) R. Breslow, *Chem. News*, 1965, **43**, 90; (*b*) R. Breslow, *Acc. Chem. Res.*, 1973, **6**, 393.
2 A. Mehlhorn and J. Fabian, *J. Mol. Struct.* (*Theochem*), 1984, **109**, 27.
3 (*a*) N. Tyutyulkov, B. Kurtev, Yu. Stefanovsky, F. Dietz, J. Fabian, A. Mehlhorn, G. Olbrich and O. E. Polansky, *J. Mol. Struct.*, 1985, **114**, 279; (*b*) J. Fabian, A. Mehlhorn and N. Tyutyulkov, *J. Mol. Struct.*, 1987, **151**, 355.
4 N. L. Bauld and J. Cessac, *J. Am. Chem. Soc.*, 1977, **99**, 8140.
5 N. L. Bauld, T. L. Welsher, J. Cessac and R. Holloway, *J. Am. Chem. Soc.*, 1978, **100**, 6920.
6 N. L. Bauld, *Isr. J. Chem.*, 1980, **20**, 319.
7 E. R. Davidson and W. T. Bordon, *J. Chem. Phys.*, 1977, **67**, 2191.
8 W. T. Bordon and E. R. Davidson, *J. Am. Chem. Soc.*, 1979, **101**, 3771.
9 W. J. Hehre and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1973, **95**, 5837.
10 H.-J. Köhler and H. Lischka, *J. Am. Chem. Soc.*, 1979, **101**, 3479.
11 A. Mehlhorn and J. Fabian, *J. Mol. Struct.*, 1984, **109**, 27.
12 N. Tyutyulkov, B. Kurtev, Yu. Stefanovsky, J. Fabian, A. Mehlhorn, F. Dietz, O. E. Polansky and G. Olbrich, *Comm. Dep. Chem. Bulg. Acad. Sci.*, 1985, **18**, 318.
13 M. Rabinovitz, Proceedings of the Jerusalem Symposia on Quantum Chemistry and Biochemistry, Vol. III, p. 208, The Israel Academy of Sciences and Humanities, 1971 and references cited therein.
14 A. W. Zwaard, A. M. Brower and J. J. Mulder, *Rec. Trav. Chim. Pays-Bas*, 1982, **101**, 137.
15 (*a*) M. P. Cava and M. J. Mitchell, *Cyclobutadiene and Related Compounds*, Academic Press, NY, 1967; (*b*) G. Maier and U. Mende, *Tetrahedron Lett.*, 1969, 3155; (*c*) G. Maier, W. Mayer, C. Haacke and R. Askani, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 1016; (*d*) O. L. Chapman, C. L. McIntosh and J. Pacansky, *J. Am. Chem. Soc.*, 1973, **95**, 614.
16 R. Gompper and H.-U. Wagner, *Angew. Chem.*, 1988, **100**, 1493 and references cited therein.

17 R. Gompper and G. Seybold, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 824.

18 (*a*) J. F. M. Oth, E. P. Woo and F. Sondheimer, *J. Am. Chem. Soc.*, 1973, **95**, 7337; (*b*) K. Müllen, Chem. Rev., 1984, **84**, 603; (*c*) M. Rabinovitz, I. Willner and A. Minsky, *Acc. Chem. Res.*, 1983, **16**, 298; (*d*) Y. Cohen, A. Y. Meyer and M. Rabinovitz, *J. Am. Chem. Soc.*, 1986, **108**, 7039; (*e*) A. Minsky, A. Y. Meyer and M. Rabinovitz, *Tetrahedron Lett.*, 1982, **23**, 5351; (*f*) A. Minsky, A. Y. Meyer, R. Poupko and M. Rabinovitz, *J. Am. Chem. Soc.*, 1983, **106**, 2164; (*g*) A. Minsky, A. Y. Meyer and M. Rabinovitz, *Tetrahedron*, 1985, **41**, 785.

19 H. F. King and M. Dupuis, *J. Comput. Phys.*, 1976, **21**, 144.

20 M. Dupuis and H. F. King, *Int. J. Quantum Chem.*, 1977, **11**, 613.

21 M. Dupuis and H. F. King, *J. Chem. Phys.*, 1978, **68**, 3998.

22 H. Tatewaki and S. Huzinaga, *J. Comput. Chem.*, 1980, **1**, 205.

23 C. A. Coulson and A. Golebiewsky, *Proc. Phys. Soc.*, 1961, **78**, 1310.

24 N. N. Tyutyulkov and V. Monev, *Compt. Rend. Acad. Sci. Bulgar.*, 1985, **38**, 1513.

25 J. Smid, in *Ions and Ion Pairs in Organic Reactions*, ed. M. Szwarc, Wiley-Interscience, New York, 1972, ch. 3.

26 W. König, *Angew. Chem.*, 1925, **38**, 743, 868.

27 L. G. S. Brooker, *Rev. Mod. Phys.*, 1942, **14**, 275.

28 G. N. Lewis and M. Calvin, *Chem. Rev.*, 1939, **25**, 273.

29 J. R. Platt, *J. Chem. Phys.*, 1956, **25**, 273.

30 R. Gompper and H. Glöckner, *Angew. Chem.*, 1984, **96**, 48.

31 N. N. Tyutyulkov and M. Y. Tasseva, *Compt. Rend. Acad. Sci. Bulgar.*, 1985, **38**, 871.

32 R. Gompper and T. Gessner, *Angew. Chem.*, 1985, **97**, 996.

33 R. Gompper, *Bull. Soc. Chim. Belg.*, 1983, **92**, 781.

34 R. Gompper and K. Bichlmayer, *Angew. Chem.*, 1979, **91**, 170.

35 R. Gompper and M. Junius, *Tetrahedron Lett.*, 1980, **21**, 2883.

36 R. Gompper, R. Guggenberger and R. Zentgraf, *Angew. Chem.*, 1985, **97**, 998.

37 J. F. Reimanis and J. G. Vanag, *Zh. Obchei Khim.* (*USSR*), 1975, **31**, 161.

38 B. Grimm and S. Dähne, *J. Prakt. Chem.*, 1975, **317**, 161.

39 H. Kurreck and W. Broser, *Chem. Ber.*, 1965, **98**, 11.

40 R. Breslow, *Pure Appl. Chem.*, 1982, **54**, 927.

41 K. Hafner, *Pure Appl. Chem.*, 1982, **54**, 939.

42 T. Eicher and M. Urban, *Chem. Ber.*, 1980, **113**, 408.

43 T. Eicher, F. Abdesaken, G. Franke and J. L. Löber, *Tetrahedron Lett.*, 1975, 3915.

44 N. Tyutyulkov, M. Tasseva and E. Georgiev, *J. Prakt. Chem.*, 1987, **329**, 780.

45 G. E. Ficken and J. D. Kendall, *Chimia*, 1961, **15**, 110.

46 A. D. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 1954, 2134.

47 A. C. Barker and C. Barker, *J. Chem. Soc.*, 1945, 1307.

48 A. Ya. Ilchenko, R. E. Kovalchik and L. M. Yagupolskii, *Zh. Org. Khim.* (*USSR*), 1973, **9**, 1744.

49 N. Tyutyulkov, I. Kavrakova, P. Nikolov and F. Dietz, *Z. Naturforsch., Teil B*, 1989, **44**, 1451.

50 G. Raddelien, *Chem. Ber.*, 1910, **43**, 2476.

51 A. Kliegl, *Chem. Ber.*, 1910, **43**, 2488.

52 E. A. Agracheva, L. N. Kirichenko and V. F. Gachkowski, *Zh. Obchei Khim.* (*USSR*), 1974, **44**, 1303.

53 M. Klessinger and W. Lüttke, *Tetrahedron*, 1963, **19**, Suppl. 2, 315.

54 M. Klessinger, *Tetrahedron*, 1966, **22**, 3355.

55 W. Wille and W. Lüttke, *Angew. Chem.*, 1971, **83**, 853; *Liebigs Ann. Chem.*, 1980, 2039.

56 S. Dähne and D. Leupold, *Theor. Chim. Acta* (*Berl.*), 1965, **3**, 1.

57 S. Dähne, *J. Signalaufz. Mater.*, 1984, **12**, 75.

58 J. Fabian and H. Hartmann, *Light Absorption of Organic Colorants*, Springer-Verlag, Berlin, Heidelberg, New, York, 1980.

59 N. Tyutyulkov, G. Olbrich and F. Dietz, *J. Inform. Record. Mater.*, 1988, **16**, 431.

60 E. A. Gribova, *Compt. Rend. Acad. Sci. USSR*, 1955, **102**, 279.

Paper 2/05081A
Received 23rd *September* 1992
Accepted 23rd *October* 1992