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The Chromophore of Fulvenoid Dyes

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SUMMARY

The series of pentafulvenoid dyes has recently been enriched by the deeply coloured 1,2,3,4-tetrachloro-pentafulvene-6,6-dicarbonitrile, the first representative of the 6,6-di-acceptor-substituted fulvenes. This synthesis has initiated a study of the relationships between colour and constitution of 6,6-diamino- and 6,6-dicyano-pentafulvene, cyclopentadienone and the cyclopentadienon-immonium ion. The main tool of this study was the molecular orbital and configuration analysis method according to Baba, Takemura and Suzuki within the framework of the variable β Pariser–Parr–Pople method. A clear interpretation has been achieved in terms of both iso-π-electronic delocalized and localized reference structures.

1. INTRODUCTION

The availability of various pentafulvenoid dyes prompted Griffiths and Lockwood to calculate the wavelengths of their colour bands.[1] The

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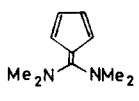
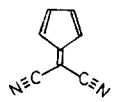
experimental absorption wavelengths of 6-amino- and 6-(*p*-aminoaryl)-substituted fulvenes and related compounds were well reproduced by Pariser–Parr–Pople (PPP) calculations. The same holds for 6,6-donor-substituted fulvenes, such as (**1**).[2] The PPP method is an appropriate approach for colour prediction[3] and for describing relationships between colour and constitution.[4,5]

Junek and co-workers recently succeeded in preparing the first representative of 6,6-di-acceptor-substituted fulvenes, namely the 1,2,3,4-tetrachloro derivative of pentafulvene-6,6-dicarbonitrile (**2**).[6]



(**1**)

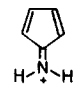


(**2**)

(**3**)

(**4**)

(**5**)



(**6**)

The spectrum of tetrachloro-(**2**) is sharply distinguished from that of (**1**) both in shape and position of the colour band. The 6,6-acceptor-substituted compound absorbs at a considerably longer wavelength than the 6,6-donor-substituted one. However, apart from the bathochromic shift, the spectrum of tetrachloro-(**2**) was found to be similar to pentafulvene (**3**).

A bathochromic shift relative to (**3**) is also observed when the exocyclic carbon atom of (**3**) is replaced by the more electronegative nitrogen, e.g. on passing from 6-phenylfulvenes to *N*-phenyl-6-azafulvenes.[1] In addition, the phenyl-substituted cyclopentadienones (tetracyclones) are more bathochromic than fulvenes.[7] An extremely long wavelength absorption is anticipated for the cationic **6**.[8]

A theoretical study of externally substituted fulvenes such as (**1**) and (**2**) and internally substituted fulvenes such as (**4**)–(**6**) can be confined to deriving data and spectral shifts. Then each conjugated system defines an individual chromophore and colour–structure relationships arise exclusively from the consideration of the change of the numerical data. The theoretical study can also be directed towards the derivation of the basic chromophoric system of the whole series considered and, thus, towards the origin of the colour in terms of the basic chromophore.

According to the classification of UV–VIS absorption bands[9] three types of basic chromophore can be distinguished.[10]

(i) In one of these, a part of the conjugated system is mainly responsible for the colour. Then the ground and lowest energy electronic states (or the electronic transition between the two

states) are localized to a certain degree. This is the locally excited chromophore (*LE-chromophore*). The heuristic value of the basic chromophore has been convincingly demonstrated by Klessinger and Lüttke in the interpretation of the indigo chromophore.[11,12] However, the basic chromophore is defined by the wavefunction rather than by the transition energy.[13]

(ii) Another type of basic chromophore is characterized by an electron transfer from one part to another of the conjugated system (*CT-chromophore*). Since the energy of the one-electron transition is given by the equation

$$\Delta E = \varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}} - J_{ij} + 2K_{ij}$$

this energy is low for CT transitions. In that case both the difference between the frontier orbitals ($\varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}}$), and the electron repulsion integral, K_{ij}, are small. On this basis, Michl and Thulstrup explained the blue colour of azulene, assuming a charge transfer from the five-membered to the seven-membered ring.[14] Pure CT transitions have not only zero K_{ij} values but also zero transition probabilities. However, in practice, the donor and acceptor fragments overlap. The oscillator strengths increase both with the squared overlap integral and distance.[15] A marked admixture of LE-type excitation may confer relatively high transition probabilities to intramolecular CT transitions, as is shown in the case of cationic dyes.[16]

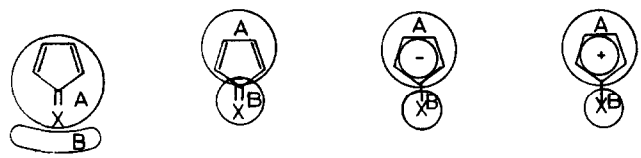
(iii) A chromophoric system may be repeated twice or several times in a conjugated system. Then the localized electron transitions interact as described according to the molecular exciton theory (*Ex-chromophore*). This effect has been extensively studied in the field of cyanine dyes.[17,18]

Inspection of the formulae (**1**)–(**3**) suggests that the pentafulvene (**3**) might be the most suitable reference chromophore system, for all the compounds are either externally or internally substituted fulvenes (Scheme 1: Model I). This approach has to provide an explanation for the fact that the spectrum of tetrachloro-(**2**) is closely related to (**3**) while the same does not hold for (**1**).

A completely different approach involves dividing the fulvenoid molecules into two fragments: *cis*-butadiene and the residue of the molecule (Model II). Fulvene can thus be considered to consist of butadiene and

ethylene.[19] This fragmentation mode may give an explanation of the colour of pentafulvenoid dyes in terms of the intramolecular CT-chromophore if the molecular parts act either as an electron donor or an electron acceptor.

However, the longest wavelength absorptions of (3) and tetrachloro-(2) are weak, suggesting that some CT occurs upon excitation.



Model I Model II Model III/1 Model III/2

Scheme 1. Different fragmentation models for the structures (1)–(6).

A rather bold fragmentation of (1)–(6) consists of dissecting the structures (1)–(5) into five-membered rings and exocyclic residues (Model III). Depending on the electron occupation of the participating ring, one may have the aromatic anion (Model III/1) or the antiaromatic cation (Model III/2). In the case of Model III/1 structure (1), for example, consists of a monomethine streptocyanine and the cyclopentadienyl anion, whereas in the case of Model III/2 (6) is described by the amino group and the corresponding Jahn Teller distorted cyclopentadienyl cation.

(1a) (6b)

The calculated geometry of (6)[8] reflects the molecular structure of (6a) quite well.

2. THE COMPUTATIONAL METHOD

The calculations were carried out according to the Pariser–Parr–Pople SC_β method, allowing an iterative correction of the carbon–carbon resonance integrals β_{CC} depending on the carbon–carbon π-bond order p_{CC} according to the equation[20]

$$\beta_{CC} = -2{\cdot}318 \exp(0{\cdot}414 p_{CC} - 0{\cdot}276)$$

The validity of this equation is somewhat restricted by the fact that the single bond length between two trigonal carbon atoms is defined to 151·7 pm. More recent results[8] suggest that this limiting value will be markedly exceeded for some of the bond lengths of the molecules considered in this paper. However, additional calculations show that neither the numerical data nor the interpretation are affected by the fact that the above mentioned equation is not strictly valid. Whereas the variation of the carbon–carbon resonance integrals has to be taken into account, an idealized geometry of the molecule is fully sufficient for calculating the electron–nucleus and electron–electron interactions. The five-membered ring was presumed to be a regular pentagon, with the exocyclic bonds of the ring forming angles of 126°. The remaining bond angles are 120° and 180°, as appropriate. All parameters employed correspond to those used in our group during the last 15 years. Since the data are scattered over several papers they are assembled in Table 1. As demonstrated with tetrachloro-(**2**) (*vide infra*), any change in the parameterization has only a minor effect on the numerical data or on the interpretation of the spectral absorptions.

The configuration interaction treatment takes into account all mono-excited configurations.

There are different methods for the interpretation of spectral transitions[21] which produce definite indices. Although most of them have no direct experimental counterparts, they provide some insight into the nature of the electron transition and have been used for classification purposes. Among various more-or-less equivalent approaches of this kind[21,22] the analytical approach of Ohta, Kuroda and Kunii[23] (hereafter termed the OKK analysis) provides the more rapid access to such

TABLE 1
PPP Parameters

Bond type (X—Y)	*R (XY)* (*pm*)	β_{XY}/β_0[a] (*eV*)	U_X (*eV*)	γ_{XX} (*eV*)
C—C	140	1·0	−11·42	10·84
C—NMe_2	140	1·0	−21·22	12·98
C≡N	115	1·3	−14·18	12·52
C=O	122	1·2	−17·28	14·58
C—Cl	170	0·55	−24·01	11·27

[a] $\beta_0 = -2{\cdot}318$ eV.

data. Each transition is characterized by the locally excited contributions of the molecular fragments and charge-transfer contributions between the fragments. In contrast to the usually considered unilateral (total) electron transfer between any two fragments, the charge transfer of the OKK analysis distinguishes between transfer in the forward and backward direction. The analysis of Baba, Suzuki and Takemura[24] (hereafter called the BST analysis) differs markedly from the former in three ways: (i) electronic states rather than electronic transitions are considered; (ii) the consideration is not restricted to a molecular fragmentation but enables comparison between iso-π-electronic systems as well; (iii) the deductive BST analysis paves the way for an interpretation based on an inductive approach by using the quantitative Longuet-Higgins–Murrell (LHM) method[25] or by using the qualitative perturbational MO (PMO) theory.[26] The comparison between iso-π-electronic ('isoconjugated') systems and the concept of molecular building blocks are the *sine qua non* of any interpretative UV spectroscopy.[27] The BST analysis is the most appropriate mathematical tool for this.[28]

3. RESULTS AND DISCUSSION

3.1. The absorption spectra of 1,2,3,4-tetrachloro-pentafulvene-6,6-dicarbonitrile and of the various pentafulvenes

As shown in Table 2, the absorption wavelengths are excellently reproduced by the PPP–SC_β calculations. The calculations suggest that the first and second absorption maximum found experimentally belong to $\pi \rightarrow \pi^*$ transitions. Adapting the standard parameter set, the two longest-wavelength absorptions of tetrachloro-(**2**) are calculated to be 162 and 64 nm more bathochromic than pentafulvene (**3**). This is in good agreement with the shifts of 179 and 78 nm found experimentally. Quite similar spectral data are obtained when a parameter set is used which has been optimized for nitrile-substituted aromatics.[29] As shown by the results reported in Table 2 the conventional PPP method with fixed resonance integrals completely fails in predicting the colour band, because the compound displays a pronounced bond alternation. Consideration of the bond alternation leads to a pronounced hypsochromic shift of the colour band from the near infrared to the visible region.

TABLE 2

Theoretical and Experimental Absorption Wavelengths (in nm) of 1,2,3,4-Tetrachloro-pentafulvene-6,6-dicarbonitrile

Log values of the theoretical oscillatory strength and log values of the experimental molar absorptivity are given in parentheses

	PPP[a]	*PPP-SC*$_\beta$[b]	*Experiment*
Parameter set 1[c]	867 (−2·10)	530 (−2·11)	541 (2·14)[e]
	538 (0·00)	313 (−0·03)	306 (4·37)
Parameter set 2[d]	956 (−2·25)	567 (−2·11)	541 (2·14)
	354 (−0·02)	306 (−0·08)	320 (4·40)

[a] Fixed β_{CC} values.
[b] Variable β_{CC} technique.
[c] Parameters collected in Table 1.
[d] Parameters proposed in Ref. 29.
[e] In cyclohexane.[6]

Due to use of the standard PPP–SC$_\beta$ method with exclusion of multiply excited configurations, experimental oscillator strengths f of weaker transitions cannot be reproduced satisfactorily.[3,30]† Therefore, the discussion in this paper is restricted to a qualitative comparison of the theoretical $\log f$ and experimental $\log \varepsilon$ values which are roughly proportional to each other ($\log \varepsilon = \log f + 5$). The entries in Table 2 correctly indicate a weak first and intense second absorption. The spectral transitions for the whole series (**1**)–(**3**) and (**5**)–(**6**) are presented in Table 3. The general characteristics are the same for all compounds: i.e. a weak low energy transition is followed by an intense higher energy transition. In the case of 6,6-diamino-substituted pentafulvene, both transitions have nearly the same energy and give rise to a single absorption band. This corresponds to the experimental findings.[6,31]

The prediction of the absorption wavelengths of the compounds (**2**), (**3**), (**5**) and (**6**) also appears to be quite reasonable (cf. Table 3). In the case of (**1**) the experimental value is closely reproduced. Compound (**2**) should absorb weakly at some 80 nm and intensively at some 10 nm shorter wavelength than 1,2,3,4-tetrachloro-pentafulvene-6,6-dicarbonitrile. Compound (**5**) is highly unstable and undergoes dimerization below 80 °C.[32] Substituted compounds are known, but due to the substituent effects, they absorb at longer wavelengths than predicted for the parent compound (cf. Table 3). The synthesis of the highly bathochromic

† Experimental and theoretical f values of pentafulvene have been juxtaposed in Ref. 1.

TABLE 3

Calculated Transition Energies, One-Electron Transition Energies and Their Partitioning (in eV) and Theoretical and Experimental Absorption Wavelengths (in nm)

Compound	ΔE_1 (log f_1) ΔE_2 (log f_2)	$\%_{o(1\to1')}$ $\%_{o(2\to1')}$	$\Delta E_{(1\to1')}$ $\Delta E_{(2\to1')}$	$\Delta\varepsilon_{(1\to1')}$ $\Delta\varepsilon_{(2\to1')}$	$J_{11'}$ J_{21}	$2K_{11'}$ $2K_{21}$	λ_1^{calc} λ_2^{calc}	λ_1^{exp}(log ε) λ_2^{exp}(log ε)
(1)	3·58 (−1·53)	98·9[a]	3·45	6·72	4·18	0·91	345	342 (4·44)[c]
	3·64 (−0·18)	97·0[b]	3·92	6·90	4·53	1·55	341	
(2)	2·73 (−1·90)	98·8	2·80	6·36	4·44	0·88	453	541 (2·14)[d]
	4·12 (−0·02)	96·5	4·23	6·74	4·79	2·28	301	320 (4·40)
(3)	3·37 (−1·46)	99·2	3·44	7·05	4·97	1·37	368	362 (2·33)[e]
	4·97 (−0·23)	93·6	5·26	7·79	5·52	2·99	249	242 (4·1)
(5)	2·95 (−1·72)	97·9	3·06	6·96	5·30	1·39	419	390 (2·43)[f]
	5·35 (−0·54)	78·8	5·84	8·62	5·71	2·93	291	210 (3·86)
(6)	1·40 (−3·88)	99·5	1·43	5·69	5·00	0·74	883[g]	
	4·45 (−0·39)	93·9	4·80	7·53	5·40	2·68	279	

[a] $2\to1'$ transition.
[b] $1\to1'$ transition.
[c] In hexane.[31]
[d] 1,2,3,4-Tetrachloro-(**2**) in cyclohexane. Results of the calculation of the tetrachloro derivative: cf. Table 2.
[e] In cyclohexane.[34]
[f] 3,5-Di-*tert.*-butyl-(**5**) in isooctane.[35]
[g] 792 and 278 nm according to PPP calculations with β_{CC} resonance integrals calculated from MINDO/3-optimized C—C bond lengths.

(**6**) may be more difficult because it represents a singly donor-substituted antiaromatic cyclopentadienyl. Because of the long absorption wavelengths of (**6**) the numerical result might be sensitive to structural modifications. The PPP calculation of (**6**) has been repeated. The carbon–carbon resonance integrals were derived from the relationship

$$\beta = -2{\cdot}318 \exp\left[0{\cdot}023(R_{calc} - 139{\cdot}7)\right]$$

from the bond lengths (in pm) obtained by MINDO/3 geometry optimizations[8] (cf. footnote *g* to Table 3). Since the bond alternation is now stronger than in the variable β PPP calculations the colour band is now predicted at shorter wavelength. The spectral pattern, however, is unchanged.

With the exception of (**1**) the first band of fulvenoid dyes is an almost pure transition between the uppermost filled MO and lowest free MO ($1\to1'$ transition) of the type $1A_1 \to 1B_1$, i.e. the transition is polarized perpendicular to the twofold symmetry axis. The second band results from electron excitation from the subjacent filled MO to the lowest energy

TABLE 4

Contribution of Local Excitation (LE) and Charge-Transfer Excitation (CT) to the Lowest Energy Transition $1A_1 \rightarrow 1B_2(1)$ and the Subsequent Transition $1A_1 \rightarrow 2A_1(2)$ (OKK Analysis)

Model	*Compound*	*Transition*	*Percentage*			
			LE_A	$CT_{A\rightarrow B}$	$CT_{B\rightarrow A}$	LE_B
II	(1)	1	29	71	—	—
		2	14	31	16	39
II	(2)	1	35	65	—	—
		2	14	20	23	43
II	(3)	1	50	50	—	—
		2	29	20	25	16
II	(5)	1	53	45	—	—
		2	48	24	16	13
II	(6)	1	40	60	—	—
		2	34	38	11	17
III	(1)	1	30	70	—	—
		2	25	55	6	13
III	(2)	1	52	48	—	—
		2	30	26	23	21
III	(3)	1	61	39	—	—
		2	46	23	19	12
III	(5)	1	76	24	—	—
		2	62	14	18	6
III	(6)	1	79	21	—	—
		2	59	13	22	6

MO ($2 \rightarrow 1'$ transition) and is labelled as a $1A_1 \rightarrow 2A_1$ transition. This transition is therefore aligned along the symmetry axis. According to the results of the analysis listed in Table 3 the predominance of the $2 \rightarrow 1'$ excitation occurs only for the transition of (**5**). Because of the almost pure transitions the transition energies are mostly decreased no more than 0·3 eV by configuration interaction. Thus, the energy of the single excitations $1 \rightarrow 1'$ or $2 \rightarrow 1'$ can be examined in terms of the individual contributions of $\Delta\varepsilon$ (orbital energy difference), J (Coulomb integral) and K (exchange integral). The results of such an analysis are quite informative. For the first transition the K values are small in all cases and are significantly lower than those of the second transition. This suggests that the first transition is of the charge transfer type. The nature of the

electronic transition can be found by inspecting the change of the charges upon excitation[22] or by one of the above-mentioned analysis techniques.[21]

The OKK analysis with respect to Model II and III (Table 4) reveals, in fact, a strong intramolecular charge transfer, which proceeds from the butadiene (Model II) or cyclopentadienyl fragment (Model III) to the remaining part of the molecule. The second transition exhibits, however, contribution of the local excitation of both fragments and a charge transfer type between the fragments in both directions. This means that the second absorption is not readily interpreted in terms of molecular fragments.

3.2. Interpretation of the spectra by analysis of the lowest energy electronic states and composite molecule approaches

By BST analysis the complete basis sets of molecular and configuration functions are projected onto those of the dissected molecule according to the fragmentation modes I, II and III/1. The calculation results in correlation diagrams on the level of both the MOs and the electronic states. Whereas the MOs can be completely reproduced by those of the reference system, this is not the case for the electronic states. This is due to the fact that only the entirety of the mono-excited states of the reference system is used and can be used for reasons of clarity. Thus, any deviation from 100% (completeness of the projection, r_M) reveals how good the model under consideration is. From the diversity of numbers obtained we refer here to the contribution of the lowest energy configurations which are either solely of the localized type as for the projection of (**5**) and (**6**) onto (**3**) according to Model I or are both of the LE and CT type in terms of molecular fragments for the other models. Table 5 summarizes some results. Interestingly, the Models I and II are of almost equal quality, whereas Model III requires an additional comment.

Since Model I refers to (**3**) the r_M-values are 100% in the case of (**3**). Whereas the iso-π-electronic (**3**) and (**5**) are still similar in electronic structure, the relation is appreciably worsened on passing from (**3**) to (**6**). The picture of internal substitution is obviously no longer well suited. Structure (**2**) can be well understood as a di-nitrilo-substituted pentafulvene and this approach should make the spectral effect clear. In contrast, the diamino-substituted pentafulvene (**1**) is electronically less closely related to pentafulvene because a marked conjugative effect from the amino groups is operative. Thus, (**2**) should be more suited for LHP-

TABLE 5

Nature of the Lowest Energy Transition $1A_1 \rightarrow 1B_2$ According to the BST Analysis of the $1A_1$ Ground and $1B_2$ Excited State[a]

Compound	*State*	*Model I*	*Model II*	*Model III/1*[b]
(1)	$1A_1$	87(NB 42, $CT_{B\rightarrow A}$ 38)	92(NB 54, $CT_{B\rightarrow A}$ 33)	96(NB 66, $CT_{A\rightarrow B}$ 27)
	$1B_2$	64(LE_A 63)	64(LE_B 24, $CT_{B\rightarrow A}$ 39)	80(LE_B 74)
(2)	$1A_1$	99(NB 85)	99(NB 80, $CT_{B\rightarrow A}$ 13)	71(NB 22, $CT_{A\rightarrow B}$ 43)
	$1B_2$	88(LE_A 73)	85(LE_A 27, $CT_{A\rightarrow B}$ 57)	45(LE_B 43)
(3)	$1A_1$	100(NB 100)	99(NB 81, $CT_{B\rightarrow A}$ 13)	73(NB 23, $CT_{A\rightarrow B}$ 39)
	$1B_2$	100(LE 100)	86(LE_A 37, $CT_{A\rightarrow B}$ 49)	48($CT_{A\rightarrow B}$ 42)
(5)	$1A_1$	100(NB 91)	99(NB 88, $CT_{A\rightarrow B}$ 11)	48($CT_{A\rightarrow B}$ 34)
	$2B_2$	96(LE_A 95)	91(LE_A 38, $CT_{A\rightarrow B}$ 54)	28($CT_{A\rightarrow B}$ 26)
(6)	$1A_1$	99(NB 77, LE_A 12)	98(NB 78, $CT_{A\rightarrow B}$ 17)	34(NB 4, $CT_{A\rightarrow B}$ 28)
	$2B_2$	87(LE_A 84)	86(LE_A 22, $CT_{A\rightarrow B}$ 64)	18($CT_{A\rightarrow B}$ 17)

[a] The values (indices r_M) indicate the degree of equivalence between the considered π-electronic system and that of the reference structure (Model I, II or III/2). The values in parentheses refer to the contribution of the ground state (NB) of the reference structure, its lowest-energy excited state (LE) of the fulvene (Model I), butadiene (Model II) and the cyclopentadienyl anion (Model III/2), respectively, and to the dominant charge-transfer configuration (CT) (contributions larger than 10% only).

[b] BST analysis of (**6**) according to Model III/2: $1A_1$ 92(NB 52, $CT_{B\rightarrow A}$ 29), $2B_2$ 70(LE_A 65).

type composite molecule calculations for the lowest-energy transition than (**1**). Similar consideration can be made for the second excited state. In the interests of brevity these data are omitted here.

For qualitative interpretations, the correlation between the MOs of the molecule considered and the fragmented molecule should be considered. According to the MO correlation diagram, which is not detailed in this paper, the key orbitals of the pentafulvene reference structure are the two highest occupied and the lowest unoccupied orbitals. Figure 1 contains the pictorial representation of these reference MOs. Inspection of these MOs enables the main effect to be understood. Di-acceptor substitution of the exocyclic CH_2 in the 6-position pushes down the LUMO (1′) but does not alter the HOMO (1)† because of its nodal properties. As a result, the $1 \rightarrow 1'$ transition energy is lowered and the first band moves to longer wavelengths. Since both the 2 and 1′ MOs are lowered, the second band is

† In the SCF scheme this is not strictly valid because both the electron–nucleus and electron–electron interactions are considered.

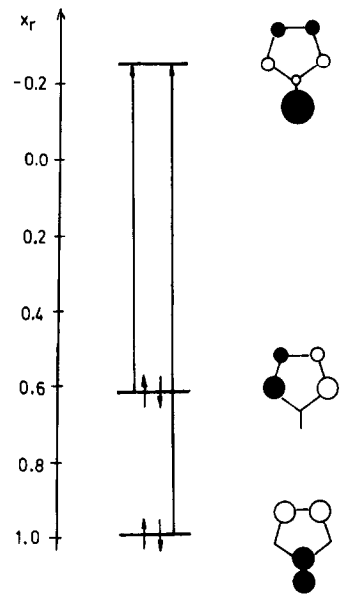
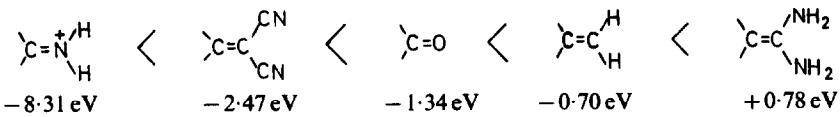


Fig. 1. Pictorial representation of the ultimately and penultimately filled MO and the lowest free MO as generated by HMO calculation. The diameter of the circular lobe is proportional to the size of the atomic orbital coefficient.

not strongly shifted. In contrast, 6-donor substitution should raise the occupied MO 2 rather than the MO 1. Thus, the differences between the transition energies for transitions $2 \rightarrow 1'$ and $1 \rightarrow 1'$ decrease. Since the common LUMO (1′) of both transitions is raised in energy the donor-substituted compound should be less bathochromic than the acceptor-substituted ones. These conclusions are completely concordant with the calculated and experimental data. Finally, substitution of the exocyclic CH_2 in the 6-position by a more electronegative element will strongly affect the $1 \rightarrow 1'$ transition energy. Because the energy of the LUMO is lowered a red shift is predicted. This explains the bathochromic shift in going from (**4**) to (**6**).

The results of the BST analysis suggest that fragmentation mode II might provide an alternative explanation of the spectral shift of the colour band in the series considered. Charge transfer from the 1,1-diaminoethene fragment to the butadiene moiety occurs in the ground state of (**1**), whereas butadiene is the donor fragment in the cases (**4**) and (**5**). The lowest-energy excited state is characterized, however, in each case by a dominant CT contribution from the butadiene donor fragment

to the residue of the molecule. According to the energy of the LUMO (Koopman's theorem) the electron acceptor strengths of this molecular residue decrease in the sequence:



This sequence in fact reflects the observed order of the absorption wavelengths. The extraordinary position of the immonium group is worth mentioning. Within the model chosen the extremely long-wavelength absorption of (**6**) is the result of a butadiene-to-immonium charge transfer. Because of the CT character, the contribution of the exchange integral to the transition energy $2K_{ij} = 0{\cdot}739$ eV is small as expected. The extremely low oscillator strengths calculated are also in full agreement with this interpretation.

Finally, the Model III/2 is only useful to a very limited extent (cf. Table 5). Structure (**1**) is well described by this model since the external donor substituents favour the cyclopentadienyl anion structure. In accordance with Dähne's structural theory[33] (**1**) is composed of an aromatic and a mono-methinic substructure (**1a**). The monomethine unit determines the lowest excited state of **1**, i.e. the colour band. This picture is less valid for **2**. The acceptor substituent opposes the formation of the cyclopentadienyl anion and the cationic polymethine structure is less favoured than in **1**. The appropriateness of Model III/1 in the case of **2** is not better than that of (**3**), the fulvene itself. Due to the electronegative exocyclic heteroatoms Model III/1 is no longer applicable for (**5**) and (**6**). Charge-transfer configurations dominate in the ground and excited states. In these cases, Model III/2 is better. It should be mentioned here that the ground and excited states of (**6**) are about 92% and 70% substituted cyclopentadienyl cation, respectively. The appropriateness of the model decreases rapidly on passing from (**6**) to (**4**). According to this approach, the extreme long-wave absorption of **6** may be attributed to the antiaromatic cyclopentadienyl cation. According to PPP-SC$_\beta$ calculations and PPP calculations, in which the resonance integrals were derived from theoretical bond lengths (geometry-optimized MINDO/3 calculations), the two Jahn–Teller distorted structures of cyclopentadienyl should absorb in the infrared (>1500 nm) and ultraviolet (~270 nm) regions.

4. CONCLUSIONS

Reference to neither the aromatic cyclopentadienyl anion nor to the antiaromatic cyclopentadienyl cation provides a clear-cut interpretation for the whole series of the fulvenoid dyes considered. The wavelengths of their colour band, which range from the near ultraviolet to the near infrared, can be understood, however, in a straightforward manner in terms of the pentafulvene chromophore. An equivalent approach involves referring to a composite molecule consisting of a butadiene residue and the internally or externally substituted *ene*. According to such a model, the position and intensity of the colour band of fulvenoid dyes are due to intramolecular CT transitions.

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