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On the Appropriateness of "Molecules-in-Molecule" Models in Describing of π-Electronic States of Composed Aromatic Systems

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Configuration analysis (CA) allows the straightforward derivation of electronic state correlation diagrams and the critical examination of the appropriateness of simple "molecules-in-molecule" approaches. The formerly thoroughly investigated fluoranthene is taken as an example. The advantage of composite-molecule approach is demonstrated by the use of energy spectra of fluoranthene analogues.

Key words: Composite-molecule approach – Longuet–Higgins–Murrell (LHM)-method – Configuration analysis (CA) – Correlation diagram – UV-VIS spectral absorption – Colour

1. Introduction

As shown by Clar [1] benzenoid hydrocarbons can retain much of their individuality when joined together to annelated systems. This fact has been supported by molecular geometries which indicate relatively long bond lengths between certain molecular fragments. Theoretical studies have led to adequate conclusions. The analysis of the one electron wavefunctions of annelated hydrocarbons in terms of localized wavefunctions (pars orbitals) enabled Polansky and Derflinger to define the relevant benzenoid fragments involved in polycyclic hydrocarbons [2].

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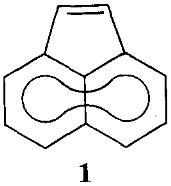
Composite-molecule approaches are very attractive for the systematization of the properties of composite molecules [3]. For interpretation purposes, the composite-molecule Longuet–Higgins–Murrell (LHM) method is therefore superior to the Pariser–Parr–Pople (PPP) method, in which the π-system as the whole is considered. However, as shown in a paper of Heilbronner, Weber, Michl and Zahradník with calculations on acenaphthylene (**1**) and fluoranthene (**2**) [4], LHM calculations can fail completely. The UV-absorption spectra of **1** and **2** are well reproduced by PPP calculations, but not by LHM calculations if only the excited states L_b, L_a, B_b and B_a of benzene and naphthalene are taken into account. Inspection of the electronic states revealed that one significant locally excited state of naphthalene is omitted in the standard LHM calculation.



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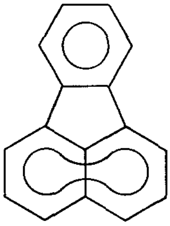

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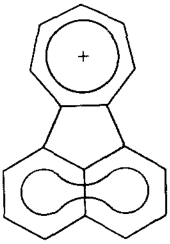
The recently developed configuration analysis (CA) of PPP wavefunctions [5] opens new avenues to "molecules-in-molecule"-type considerations [6] and should be capable of predicting any pitfall that might arise from the limited choice of the number of locally excited reference states.

Taking fluoranthene (**2**) as an example, the validity of the composite-molecule approach is examined by configuration analysis in the first part of this paper. Fluoranthene is one of the hydrocarbons the electronic spectrum of which is well-known experimentally [4, 7, 8, 10] and best reproduced theoretically [4, 7–9, 11]. Since the lowest energy electronic states are already satisfactorily calculated in the early 1966 paper [4], the fluoranthene electronic states of that paper have been subjected to the analyses.

In the second part of the paper, colour–structure relationships between fluoranthene and the iso-π-electronic structures **3**–**6** are derived in terms of molecular fragments. The ionic compounds **3** and **4** have been reported to be more deeply coloured than **2** [12, 13]. Furthermore, significant differences in the spectral feature of the isomeric sulphur heterocycles **5** and **6** and their N-methyl heteroanalogues have been found by one of the authors (M.Sch.) [14].



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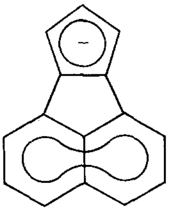

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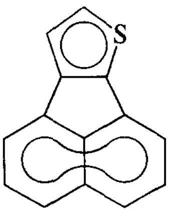

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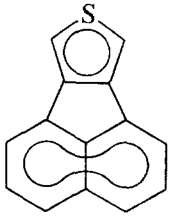

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The lower excitation energies of **3** and **4** compared with **2** might be governed by the larger acceptor and donor strength, respectively, of the 6π-electron subsystem compared with benzene (energy gap controlled bathochromicity), whereas the lower excitation energy of **5** relative to **6** might arise from the different overlap between the fragment orbitals (overlap controlled bathochromicity).

2. Configuration Analysis of the Electronic States of Fluoranthene

The PPP calculation of fluoranthene has been repeated according to model D of Ref. 4 projecting the resulting electronic wavefunctions onto the wavefunctions of fragmented molecule. Depending on the number of electronic reference states of the benzene and naphthalene subunits the completeness of the description of the fluoranthene states in terms of reference states differs markedly. If the states $L_b.L_a$, B_b and B_a only are selected for each fragment and 8 CT states (4×4 configurations according to Table 1), the description of some fluoranthene excited states is rather incomplete. As documented in Table 1, these states are reproduced to less than 60%, among them the lowest-energy excited state of fluoranthene (K-state according to Ref. 9). Consequently, composite-molecule calculations by the Longuet–Higgins–Murrell (LHM) method ("molecules-in-molecule" calculations) cannot provide the correct energy spectrum, as long as the configuration interaction is refined to the above mentioned four excited states of each

Table 1. Completeness of the projection of the lowest energy state wavefunctions of fluoranthene[a] onto the lowest energy state wavefunctions of the fragmented molecule[b]

Electronic state[c]	Number of singly-excited configurations of the fragmented molecule 4×4	5×5	6×6
S_0	86	90	92
S_1 (K)	45	72	74
S_2 (L)	77	78	80
S_3 (M)	74	76	78
S_4 (N)	70	75	77
S_5	29	64	74
S_6	57	79	80
S_7	51	71	73
S_8	77	78	79

[a] Standard PPP calculation D in Ref. 4, calculation A in Ref. 8. Both for **2** and the fragmented molecule the geometry assumed in the calculations consisted of three regular hexagons and all bond lengths equal to 1.40 Å. The resonance integrals β_{CC} are all equal to -2.318 eV.

[b] Configuration interaction between $n\times m$ singly-excited configurations; n is the number of occupied MO's and m the number of unoccupied MO's involved in the configuration interaction.

[c] Term labels according to Ref. [9] in parenthesis.

fragment. This result supports the conclusions drawn formerly [4] by inspection of the wavefunction.

The composite-molecule description of fluoranthene becomes more complete when additional locally-excited (LE) states of the fragments and charge-transfer states (CT) are involved in the set of reference states. Already reference to the 10 lowest energy LE states of the fragments and 15 CT states (5 × 5 configurations according to Table 1) enables a reproduction, in the main, of each low-energy electronic state of fluoranthene in terms of the reference states. If these reference states are considered in the LHM calculation, the energy spectrum is essentially reproduced as well. Due to the fact that the reproduction of the fluoranthene electronic state ranges between only 70 and 80%, results of the PPP and LHM calculation (in the same parametrization) are not numerically equivalent, however, and even changes in the term level sequence have been found. Moreover, in agreement with the results of the configuration analysis assembled in Table 1, further extension of the number of singly excited configurations cannot essentially improve the results of the LHM calculations. Only inclusion of higher excited states would make the numerical results of LHM calculations more equivalent to those of the PPP calculations. But then the advantage of the LHM calculation, which consists in making results more transparent and better understandable, is completely lost.

Although configuration analysis indicates some deficiency in the composite-molecule approach in the quantitative treatment of **2**, qualitative interpretation in

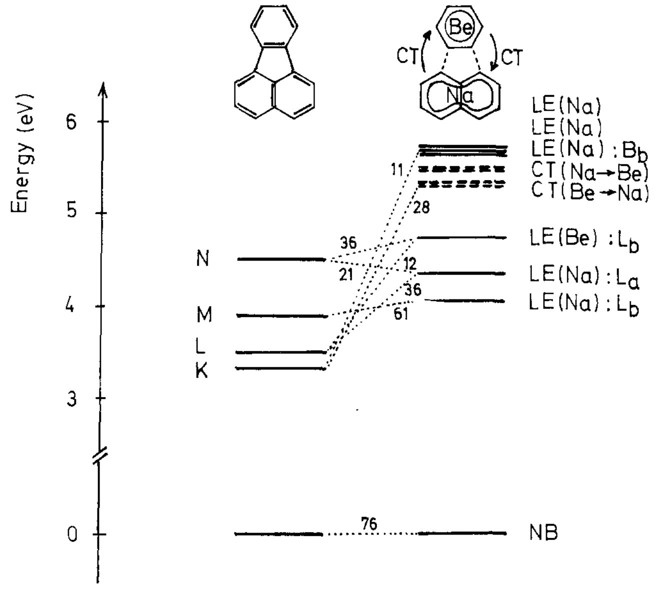


Fig. 1. State correlation diagram of the lowest energy levels of fluoranthene (**2**) and the molecular fragments benzene and naphthalene. The excited state term levels of **2** are labelled according to Ref. 9

terms of molecular fragments is justified and easily possible by the resulting correlation diagrams. Correlations between the five lowest-energy electronic states of fluoranthene and the fragmented molecule are depicted in Fig. 1. The numbers on the dotted lines are the contributions of the reference states to the electronic states of fluoranthene. According to Fig. 1 the lowest-excited state K of fluoranthene contains, besides a locally excited state of naphthalene (not considered in the former [4] LHM calculations), a dominant CT-state contribution. In the L and N states of **2**, the L_a state of naphthalene mixes with the L_b state of benzene, whereas the M state correlates closely to the L_b state of benzene.

The longest-wavelength absorption of fluoranthene is due to the electronic excitation from the ground state to the K-state. Lowering of the K-state energy relative to the ground state by structural modification will result in lower excitation energies and consequently coloured compounds. The nature of K-state suggests that lowering of the CT excitation energy between the fragments brings about longer wavelength absorptions. A pronounced bathochromic effect should therefore occur when benzene is replaced by a stronger acceptor molecule such as the tropylium ion, or a stronger donor molecule such as the cyclopentadiene anion.

3. PPP-CA Calculations on Fluoranthene Analogues

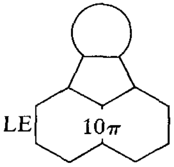
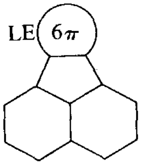
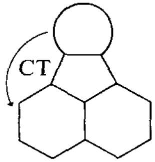
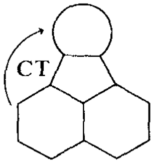
PPP calculations support the long-wavelength absorption of **3** and **4** expected from the above-mentioned composite-molecule considerations (Table 2). The lowest-energy transition energies are compatible with the orange-red colour of **3** ($\Delta E = 2.83$ eV, in acetonitrile solution) and the dark red colour of **4**, respectively. According to Table 2 the lowest-energy transitions of **2**, **3** and **4** are related. Configuration analysis of the wavefunctions in terms of molecular fragments indicates the similar nature of the excited states and in such a way reveals indirectly correlations between the iso-π-electronic structures that are not topologically equivalent. The correlation diagram cannot be obtained, however, by projecting the wavefunctions directly onto each other.

As expected, the transition energy increases when the cyclopentadiene anion is replaced by thiophene. But despite having the same molecular fragments, the calculated energy spectrum of the isomeric heterocycles is markedly different. In contrast to compound **6**, compound **5** displays a weak electronic transition at long wavelengths. The existence of this transition obviously accounts for the experimentally discovered [14] longer wavelength absorption of **5** relative to **6**.

Whereas the larger bathochromicity of **3** to **6** with respect to **2** is governed by the lower CT-transition energies between their molecular fragments (energy gap controlled bathochromicity), differences in energy between the lowest-energy transitions of **5** and **6** are determined by the difference in interfragmental overlap (overlap controlled bathochromicity).

Configuration analysis reveals the nature of the electronic state responsible for the weak electronic transitions $S_0 \rightarrow S_1$ of **5** and $S_0 \rightarrow S_2$ of **6**. These transitions are

Table 2. Nature of the three lowest-energy excited states according to PPP-configuration analyses[a]

										
Compound	ΔE in eV	(f)	Polarization[b]	r_M	$L_b(y)$	$L_a(z)$	% LE1	% LE2	% CT	% CT
2	3.36	(0.02)	y	75	4	—	—	6	28	1
	3.50	(0.52)	z	80	—	36	12	—	16	10
	3.91	(0.07)	y	78	61	—	—	1	3	7
3	2.90	(0.01)	y	68	1	—	—	8	—	45
	3.13	(0.58)	z	68	—	16	1	—	—	27
	3.33	(0.01)	y	68	17	—	—	2	—	35
4	2.05	(0.02)	y	76	—	—	—	7	54	—
	2.94	(0.67)	z	73	—	15	5	—	40	—
	3.65	(0.06)	y	70	38	—	—	—	28	—
5	2.73	(0.07)		77	1	—	—	8	38	—
	3.44	(0.58)		77	—	36	7	—	19	8
	3.83	(0.07)		78	61	—	—	—	3	7
6	3.50	(0.56)	z	83	—	39	—	—	28	5
	3.58	(0.01)	y	79	4	—	—	—	36	—
	3.89	(0.01)	y	80	64	—	—	6	9	—

[a] Completeness of description of the excited states (r_M) and contributions of important excited states of the fragmented molecules in %; 5 × 5 singly excited configurations of the molecule and 6 × 6 singly-excited states of the fragmented molecule are considered.

[b] y: polarized perpendicular to the twofold axis; z: polarized along the twofold axis.

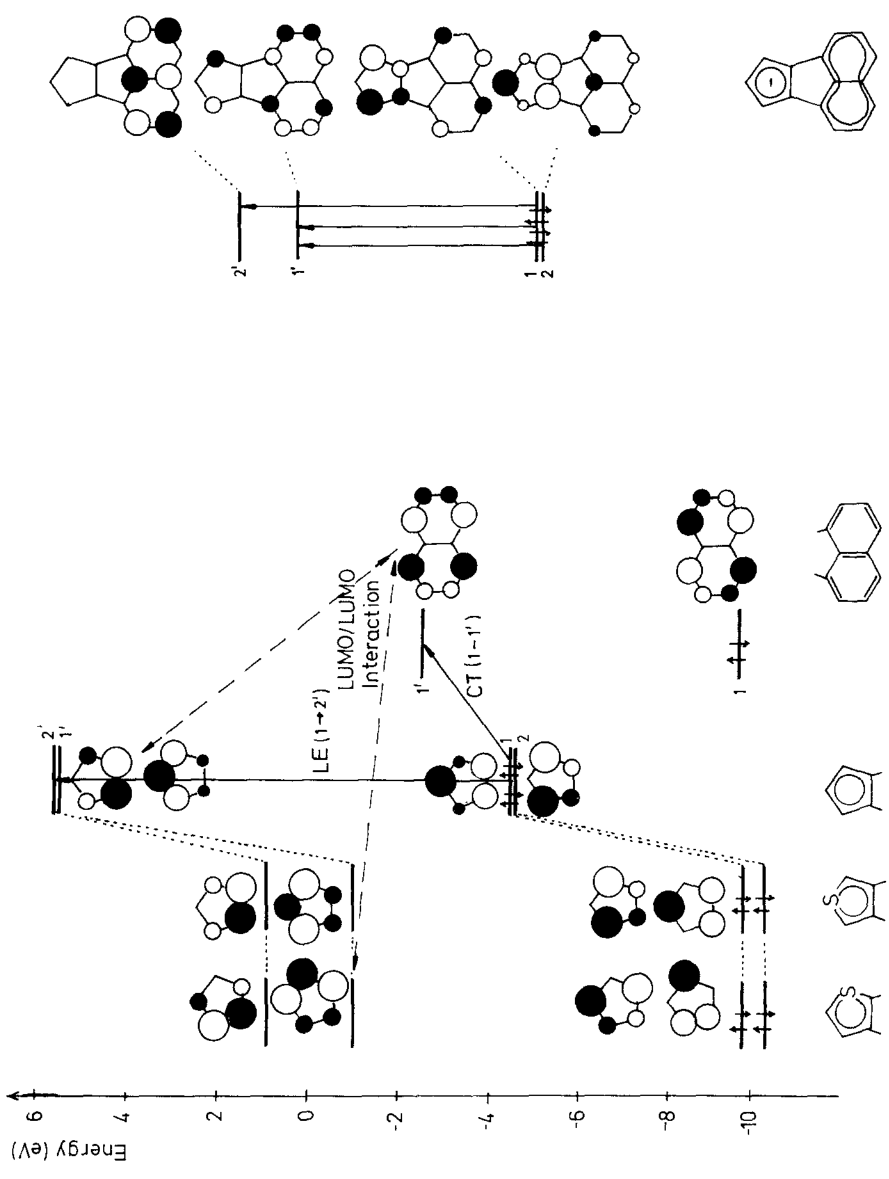


Fig. 2. Interpretation of spectral peculiarities of sulphur-heterocyclic fluoranthene analogs in terms of the fragment MO's (on the left) and in terms of the parent hydrocarbon (on the right)

governed by a thiophene-to-naphthalene charge transfer. As displayed for the corresponding lowest-energy transition of the parent hydrocarbon **4** in Fig. 2 electron transfer occurs from one of the degenerate occupied MOs of cyclopentadiene to the lowest free MO of naphthalene. This CT state interacts with the locally excited (LE) electronic state at the cyclopentadiene anion resulting from excitation from the same occupied MO mentioned above and one of its degenerate free MO's. The strength of interactions, which determines the energy of the lowest term levels is governed by the overlap between the LUMO's involved in the CT and LE transitions.

When the cyclopentadiene anion is replaced by thiophene, the degenerate LUMO's of the hydrocarbon undergo energy splitting. The lower-energy unoccupied MO is energetically favoured only for the LUMO–LUMO interaction. In the geometrical composition of **6**, the LUMO's of thiophene and naphthalene cannot interact for reasons of symmetry. Consequently, the electronic transition energy remains at relatively high energies. In the geometrical composition **5**, however, an effective LUMO-LUMO interaction is operative and the transition energy is lowered.

An equivalent explanation of the spectral difference between **5** and **6** can be obtained when considering and comparing electronic systems as a whole. The correlation diagram between **5** and **4** and **6** and **4** support correlations between the first three transitions and the alteration in the term level sequence (Fig. 3). This approach directs attention to the nature of the lowest-energy transition of **4**. This transition is mainly a one-electron transition between the second occupied MO 2 and the lowest empty orbital 1′ of **4**. According to the orbital expansion coefficients, heteroatomic substitution will considerably affect this transition 2 → 1′ on passing from **4** to **6**. Due to the dominant stabilization of the occupied

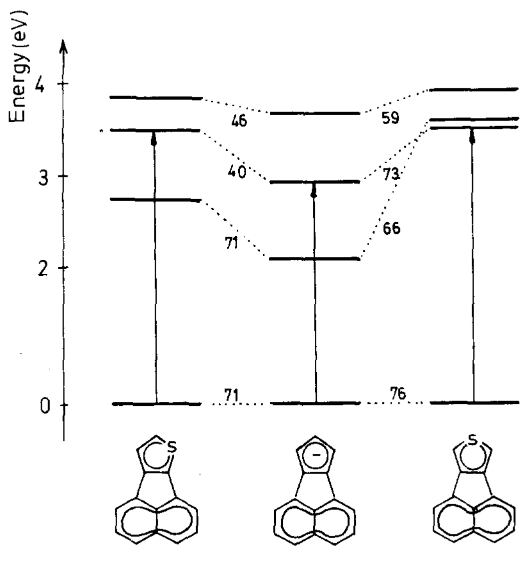


Fig. 3. State correlation diagrams between the sulphur-heterocyclic fluoranthene analogs and the hydrocarbon parent compound. Cf. caption to Fig. 1

MO, the 2 → 1′ transition is shifted to higher energies. In fact, the weak long-wavelength band of **5** is absent in **6** [14].

4. Conclusions

The PPP configuration analysis (CA) proves to be a powerful tool in checking the validity of molecular building block models ("molecules-in-molecule" models) in π-approximation. Along these lines the failure of the conventional molecule-in-molecule calculations (Longuet–Higgins–Murrell method) for fluoranthene or any other compound can easily be predicted. The analysis enables the derivation of the minimum number of locally excited states required in composite-molecule calculations. The completeness of the description of the analyzed states in terms of the fragment states determines the accuracy of such calculations.

The configuration analysis provides state correlation diagrams. They are fundamental for any comparative interpretation and systematization of spectra. Whereas the direct comparison by CA is restricted to π-electronically and topologically equivalent structures ("isoconjugated structures"), reference to molecular fragments extends the range of compounds to be compared.

Even if term levels are not sufficiently numerically reproduced by the composite-molecule approach, spectral features can be qualitatively understood. This has been demonstrated in this paper by the use of fluoranthene analogues. Their lowest-energy transitions are determined either by the energetics of the fragments (alteration of fragments) or by the orbital overlap between the fragments (alteration of the linkage between fragments). In other words, the bathochromicity of these compounds is either energy-gap or overlap controlled.

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