

## TRANSANULAR INTERACTIONS IN [2.2]PHANES – RELATION BETWEEN SPECTROSCOPIC PROPERTIES AND STRUCTURAL PARAMETERS OF [2.2]PHANES

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In this paper we attempt to explain the spectroscopic properties of a number of [2.2]phanes. All phanes discussed have in common that their two subunits are identical and that they possess the  $\pi$ -electron system of diphenyl or a larger one which includes the one of diphenyl. The crucial quantity for an understanding of the  $\pi\pi$ -interaction in phanes is the bond density  $d_{ij}^{\pi}$  between the  $2p_z$ -atomic orbitals of corresponding pairs of the aromatic C-atoms of the two subunits of a phane and its sum over all C-atoms, the total intersystem bond density  $d_T^{\pi}$ . These quantities are in general larger for an excited singlet state than for the corresponding triplet state, which leads to a relatively stronger interaction in the former. The broadening of the emission spectra of the phanes as compared to the corresponding monomers which is generally observed can be explained in terms of a Franck–Condon type of coupling due to a change in the equilibrium distance in the excited state with respect to the ground state.

### 1. Introduction

In the last years, Staab and his group have synthesized a considerable number of [2.2]phanes including diphenylophane, fluorenophane, phenanthrenophane, pyrenophane and several isomeric naphthalenophanes in order to study the transanular  $\pi\pi$ -interaction. The spectroscopic properties of these phanes were studied in several preceding papers [1–3]. A major part of the interaction between the subunits of the phanes is a  $\pi$ -electron interaction through space as in excimers [4], i.e. in an excited state one may expect the  $\pi$ -orbitals to become bonding in the same manner as they are in excimers.

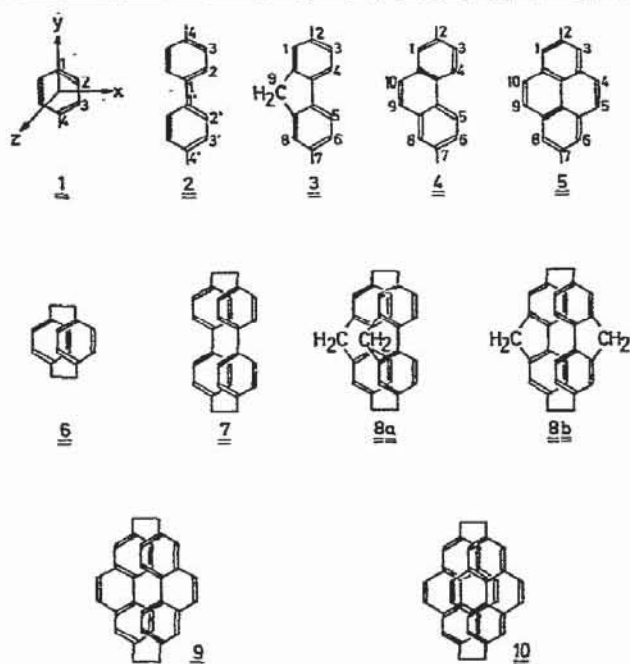
An additional aspect to be considered is the  $\sigma\pi$ -interaction. The bonding  $\pi$ -orbitals have almost the same direction and symmetry as the bonds between the two C atoms in the bridges, normally called  $\sigma$ -bonds. A complication arises from the fact that the aromatic subunits are not planar but bent to a not inconsiderable degree as we know from the X-ray structure of the

phanes. This makes a separation of  $\pi$ - and  $\sigma$ -bonds in the aromatic systems of the phanes strictly speaking impossible. Given the symmetry of some of the phanes, which is  $D_{2h}$  in good approximation [5], one might formally redefine  $\pi$ - and  $\sigma$ -orbitals. This does not take away the problem however, that one may get certain interactions which one does not encounter in simple planar non-bridged aromatic ring systems. The importance of the “through-bond” interaction versus the  $\pi\pi$ -interaction through space and  $\sigma\pi$ -interaction was discussed previously [6].

In section 2 we have compiled a number of [2.2]-phanes with identical subunits and their relevant spectroscopic data in tables 1 and 2. In addition, we quote the results of the X-ray structure analysis of some of these phanes.

In section 3 we try to give a rationale for the phenomena and their trends as observed in the phane systems collected in table 1. Rather than trying to give an exact quantum mechanical solution for the problems, which is impossible because of the complexity

Table 1  
Phanes and monomers



1,4-dimethylbenzene 1, 4,4'-dimethyldiphenyl 2, 2,7-dimethylfluorene 3, 2,7-dimethylphenanthrene 4, 2,7-dimethylpyrene 5. [2.2]paracyclophane 6, [2.2](4,4')diphenylophane 7, [2.2](2,7)fluorenophane (syn) 8a, [2.2](2,7)fluorenophane (anti) 8b, [2.2](2,7)phenanthrenophane 9, [2.2](2,7)pyrenophane 10. Coordinate-system for all monomers and phanes as shown for 1. Numbering of atoms in phanes analogous to monomers.

Table 2

Red shifts of emission spectra and reduction of  $D$  value [2.2]phanes, both with respect to the corresponding monomers. Uncertainty of shifts is due to large linewidth

[2.2]phanes	Red shift of emission			Reduction of $D$ parameter $\frac{ D_{\text{mon}}  -  D }{ D_{\text{mon}} }$ (%)	Liter.
	Fluorescence ( $\text{cm}^{-1}$ )	Phosphorescence			
		( $\text{cm}^{-1}$ )	Linewidth		
[2.2]paracyclophane 6			very broad	15 <sup>a)</sup> 24	7
[2.2](4,4')diphenylophane 7	3200 $\pm$ 400	1000 $\pm$ 400	broad	12.8	8
[2.2](2,7)fluorenophane (syn) 8a	3900 $\pm$ 300	1100 $\pm$ 200	sharp	13.8	8
[2.2](2,7)fluorenophane (anti) 8b	2600 $\pm$ 300	700 $\pm$ 200	sharp	7.8	8
[2.2](2,7)phenanthrenophane 9	1700 $\pm$ 200	600 $\pm$ 200	broad	6.5	1
[2.2](2,7)pyrenophane 10	7800 $\pm$ 200	100 $\pm$ 100	somewhat broadened	2.5	3

a) Two sets of parameters the origin of which is not clear.

of the molecules, we propose some simple physical arguments which give a certain plausibility to some of the main features of the observations. Furthermore, the experimental results are discussed in the light of these general considerations. In section 4 finally we try to draw some conclusions.

## 2. Experimental data

The formulae of the [2.2]phanes discussed in this paper as well as the corresponding monomers are given in table 1. These [2.2]phanes were selected because their subunits possess either the  $\pi$ -electron system of diphenyl (diphenylophane, fluorenophane) or a larger one which includes the  $\pi$ -electron system of diphenyl (phenanthrenophane, pyrenophane) and because in all these phanes the connecting methylene bridges are substituted in an analogous position. Paracyclophane is included as well in order to compare the properties of the larger phanes with those of a smaller one. The red shifts of the fluorescence and phosphorescence spectra as well as the reduction of the zero field splitting parameter  $D$  of these [2.2]phanes are listed in table 2. For comparison the dimethyl substituted monomers are used because their structure is as close to one half of the corresponding phane as possible. Since some of the phosphorescence spectra are rather sharp and structured, the linewidth is indicated in one column; for the spectra themselves the reader is referred to the literature [1,3,7,8].

In addition, we quote some structural parameters as obtained by X-ray structure analysis. In [2.2] paracyclophane **6** the benzene rings are slightly bent; the transannular distance between corresponding C atoms in the two rings varies from about 2.8 Å to 3.1 Å [9]. In [2.2](2,7) pyrenophane **10** due to the larger size of the system the distance between corresponding C atoms varies even more, namely from 2.79 Å at the ends to 3.80 Å in the middle [5].

An X-ray structure determination of anti-fluoreno-**8b** has recently been completed [10]. The results are fairly similar to those of pyrenophane **10**. The fluorene subunits are bent, the C atoms to which the bridges are linked have a distance of 2.79 Å. The two five-membered rings are approximately planar (except the CH<sub>2</sub> group) and parallel with respect to each other, but the C atoms are not on top of each other as shown in fig. 3 of the preceding paper [8] and the shortest distance between two C atoms in different five-membered rings is 3.82 Å, while the distance between the planes of these rings is only 3.63 Å.

### 3. Discussion

#### 3.1. General considerations

For a general background of the theory we refer the reader to some papers easily available in the literature. Firstly we make use of the extensive quantum mechanical calculations done on singlet and triplet states of a system of two benzene molecules considered as an excimer [11,12] used as a model for paracyclophanes. Secondly we refer to a general review on the photophysics of aromatic excimers with references to paracyclophanes published by Birks [13]. Thirdly a previous paper in this series [1] gives some remarks on the interaction of two aromatic systems in an excited state, in particular in connection with the charge transfer character and the *D* and *E* values ofphanes in an excited triplet state.

In the first part of the discussion we look on the properties of the singlet state, in particular its fluorescence. Both fluorescence and phosphorescence of the monomers show a sharp vibrational structure, but while the phosphorescence of thephanes varies from structureless in paracyclophane **6** to a sharp vibrational structure in the fluorenophanes **8a** and **8b**, all fluores-

cence spectra are broad structureless bands.

Vogler et al. [14] have published Hückel MO-calculations for CT-phanes. When considering the different behaviour of fluorescence and phosphorescence one must take into account that one needs different orbitals for corresponding singlet and triplet states [1]. Theory and detailed quantum mechanical calculations done for atoms [15–17], H<sub>2</sub> [16,18], C<sub>2</sub>H<sub>4</sub> [19]; C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> [20] and C<sub>4</sub>H<sub>6</sub> (trans butadiene) [21] show that the wavefunction for an excited singlet state, in SCF approximation in particular the outer orbital, is more, sometimes much more diffuse than the corresponding wavefunction or orbital in the triplet state. For details the reader is referred to the literature [15–21].

This reinterpretation of spectroscopic energy differences, which becomes necessary as a consequence of these calculations, in particular the fact that the singlet state has a considerably farther expansion in space mainly along the *z*-direction perpendicular to the plane of the aromatic system, may give a clue to the interpretation of the differences in the fluorescence and phosphorescence spectra of thephanes [1].

In general, the repulsion between the two triplet electrons is more marked in the smaller orbital (one benzene ring) in the subunit of the smaller phane paracyclophane **6** as compared to the larger subunits of the largerphanes and hence the triplet electrons tend more to be at a given time in two different rings in the smallerphanes.

Furthermore, one expects that the  $\pi\pi$ -interaction between the subunits and consequently the charge transfer (CT) terms in the wavefunction become more important when the distance between the subsystems of thephanes become smaller and that consequently increasing charge transfer terms tend to reduce the zero field splitting parameters *D* and *E* with respect to the monomers [1]. In the largerphanes, on the other hand, the average distance between the subsystems becomes larger and hence the contribution of the charge transfer terms becomes smaller. This is a further reason for the smaller reduction of the *D* parameter in the largerphanes in addition to the one mentioned above. In ref. [12] it is pointed out that the red shift of the phosphorescence in paracyclophane depends on the overlap of the triplet states in the dimer of benzene. It is concluded that "in the absence of such overlap, the transition energies would be the same as those

of benzene and would not depend upon inter-ring separation". It is mentioned further that this is in contrast to the behaviour of the dimer singlet states which show also a shift in the zero overlap approximation [12] (see the appendix).

These statements are generally true and not restricted to benzene dimers only. We observed that in general the red shift of the phosphorescence is rather small for the largerphanes and considerably larger for paracyclophane, a result which is consistent with the reduction of the  $D$  values. This indicates that for larger inter-ring distances the overlap is small and so is the red shift and the reduction of the  $D$  values, while for smallerphanes and for small distances the overlap and hence the red shift and the reduction of the  $D$  values are large. But why do we observe such different experimental results for the largerphanes compiled in table 2, why is the red shift of the phosphorescence of fluorenophane about  $1000\text{ cm}^{-1}$  and the one of pyrenophane **10** only about  $100\text{ cm}^{-1}$ , or why are the phosphorescence bands of diphenylophane **7** and phenanthrenophane **9** broad with very little structure, while the phosphorescence of both fluorenophanes **8a** and **8b** shows sharp vibrational structure?

In order to discuss the interaction between the subunits in some more detail we consider the charge density between the two subunits. The two bridges give a major contribution to this charge density, we assume, however, that this contribution is in good approximation, the same in the ground state and in the singlet and triplet excited states. Our main interest here is concentrated on the type of bonding between the subunits analogous to the bonding in excimers. The majority of the excimers were hitherto observed experimentally in the singlet state, i.e. the excimer-type of bonding is more marked in the excited singlet state than in the excited triplet state. In thephanes, however, the situation is somewhat different since the two subunits are kept together and pressed together by the methylene bridges. In order to interpret the experimental data, i.e. the red shift and the linewidth of the phosphorescence and the zero field splitting parameters, we must consider the different electron distribution in the excited singlet and triplet states as compared to the ground state.

In the appendix some general formulae are derived for charge densities and spin densities in the excited singlet and triplet states. Two consequences become

clear from these formulae:

(1) The expression for the excess charge density due to the  $\pi$ -electrons in a triplet state and in the corresponding singlet state are equal (see the appendix).

(2) The excess charge density due to the  $\pi$ -electrons and the spin density in the excited triplet state are in general not equal, but depend on the same coefficients.

Let us first consider the charge density which is the relevant quantity for dealing with energy levels and its manifestation in the experimental data, such as red shifts of the emission spectra. We are interested in the charge density due to the  $\pi$ -electrons and in particular to its part between the subunits, hence we consider only those parts which reflect the overlap between orbitals of the left hand and right hand subunit: it is given in first order by

$$-2\lambda(lr \pm LR). \quad (1)$$

The nomenclature is analogous to ref. [1], i.e.  $L$  and  $R$  are the highest occupied orbitals and  $l$  and  $r$  are the lowest unoccupied orbitals of the left and right subunit, and  $\lambda$  is a parameter which indicates the coefficient of the charge transfer terms in the total wavefunction. The upper (lower) sign is valid for excited singlet and triplet wavefunctions which are symmetrical (antisymmetrical) with respect to the plane between the subunits.

We expand the orbitals in a set of basic atomic orbitals  $\chi_i$  and  $\chi_j$  in which  $\chi_i$  denotes the orbitals for the left hand and  $\chi_j$  for the right hand subunits, so that  $L = \sum_i C_i^L \chi_i$  etc. We assume that we may use one  $2p_z$ -atomic orbital per C atom. With these definitions the total intersystem charge density (or bond density)  $d_t^\pi$  due to the  $\pi$ -electrons of the subunits becomes

$$d_t^\pi = -2\lambda \sum_{ij} (C_i^L C_j^r \pm C_i^L C_j^R) \chi_i \chi_j = \sum_{ij} d_{ij}^\pi. \quad (2)$$

We term the quantity

$$d_{ij}^\pi = -2\lambda (C_i^L C_j^r \pm C_i^L C_j^R) \chi_i \chi_j = F_{ij} P_{ij}, \quad (3)$$

the bond density for the bond between the C atom  $i$  and the C atom  $j$ . (This quantity can be considered to be a generalization of one of the expressions used in Mulliken's population analysis.) This bond between the  $2p_z$ -atomic orbitals of corresponding C atoms situated opposite to each other in the two subunits possesses cylindrical symmetry around the axes connecting these two C atoms. It is strictly speaking a  $2p_z-2p_z-$

$\sigma$ -bond although it describes an intersystem  $\pi\pi$ -interaction. It is this bond which we mean in this paper when we speak of excimer-type bonding or shortly of bonding between the two subunits in addition to the  $\sigma$ -bonds of the methylene bridges.

In order to have a convenient short-hand notation, we may write in (3)  $d_{ij}^{\pi}$  as a product of the two quantities  $F_{ij}$  and  $P_{ij}$ , where  $P_{ij} = \chi_i \chi_j$ . The definition of  $F_{ij}$  follows from (3), it measures the probability of a  $\pi$ -electron to be present in a given pair of  $2p_z$ -atomic orbitals. The bond density  $d_{ij}^{\pi}$  between C atom  $i$  and C atom  $j$  is non-zero (appreciable) only if both quantities  $F_{ij}$  and  $P_{ij}$  do not vanish (are not very small).

$P_{ij}$  is essentially a geometrical quantity which measures the extension of the  $2p_z$ -atomic orbitals in space and their relative position and distance. Since the extension of the singlet orbitals in space in the  $z$  direction can be considerably larger than the one of the corresponding triplet orbitals as mentioned above,  $P_{ij}$  might well be non-zero for the singlet state, but vanish for the corresponding triplet state. In general,  $P_{ij}$  will have finite values only for those atoms which are in opposite or approximately opposite position with respect to each other.

In thephanes shown in table 1 which consist of two identical alternant aromatic-hydrocarbons with  $D_{2h}$  symmetry (the same is true for the syn-form of the others) the values for  $C_i^L C_j^R$  and  $C_i^R C_j^L$  are equal when  $i$  and  $j$  refer to opposite C atoms. It follows from eq. (3) that in this case  $F_{ij}$  vanishes for the symmetrical wavefunction.

A further quantity which is important in this context is the spin density  $\rho_i$  and  $\rho_j$  at the C atoms  $i$  and  $j$ , respectively, because it can be measured experimentally: it is known for all monomers listed in table 1 (and hence to a very good approximation for the subunits of the correspondingphanes). The spin density is related to the same coefficients of the wavefunction as the bond density  $d_{ij}^{\pi}$  but in a different manner as outlined in the appendix. This has an important consequence, which is valid for allphanes discussed here and in general forphanes which consist of two identical alternant hydrocarbons. If one of the coefficients in eqs. (A4) and (A5), say  $L$ , vanishes at one particular C atom  $i$ , it follows from the symmetry of the system that  $R$  vanishes also at the corresponding C atom  $j$ , and the coefficients  $l$  and  $r$  of the excited states vanish as well. If all these four coefficients are zero, eqs. (A4)

and (A5) tell us that the bond density  $d_{ij}^{\pi}$  becomes zero as well as the spin density which is explained in more detail in the appendix. The same is true if these quantities are small or large. Hence the values of the spin density  $\rho_i$  and  $\rho_j$  known experimentally allow us to draw conclusions on the bond density  $d_{ij}^{\pi}$ .

When discussing the zero field splitting parameters  $D$  and  $E$  we should keep in mind that they are proportional to the dipole-dipole interaction between the two triplet electrons and hence to  $\langle 1/r^3 \rangle$ , i.e. the average over the inverse distance to the third power. Hence they decrease with increasing size of the orbitals of these two electrons. For the special case of the [2.2]phanes with two identical subunits, the comparatively small reduction found experimentally for the zero field splitting parameters of the order of 3 to 25% indicate that the two triplet electrons have a high probability to be in the same half of the phane at a given time (in contrast to the behaviour of charge-transferphanes where  $D$  value reductions up to a factor of four were observed [22]).

The reduction of the  $D$  parameter in the [2.2]-phanes discussed here as compared to the corresponding monomers depends on the total intersystem charge density  $d_{\text{t}}^{\pi}$ ; i.e. the higher  $d_{\text{t}}^{\pi}$  is, the smaller we expect  $D$  to be.  $E$  vanishes if there is at least one more than twofold axes of symmetry in the molecule. It is frequently said to measure the deviation from axial symmetry, but, of course, it decreases with increasing average distance between the two triplet electrons as well. We shall not discuss  $E$  any further and restrict ourselves to  $D$ .

Let us now discuss the spectroscopic properties of thephanes compiled in table 2 in the light of these theoretical considerations.

### 3.2. The singlet state. Fluorescence

The observation that the red shift in fluorescence is always larger than in phosphorescence finds easily an explanation in the fact that, firstly, the excited singlet state gives already a shift even if there is no overlap [12], secondly, the shifts become larger when there is overlap [11, 12], and thirdly, the outer orbitals of the singlet state of each subunit extend farther out in space resulting in a larger overlap between the singlet  $\pi$ -orbitals of the two subunits in the phane. This larger overlap leads to a stronger  $\pi\pi$ -interaction in the singlet

state than in the triplet state and hence to a considerably larger red shift.

The broad fluorescence bands without vibrational structure generally observed with complexes and excimers are usually attributed either to the random orientation of the two parts with respect to each other, or, in particular in the case of excimers, to the dissociation in the ground state. The phanes, on the other hand, possess a well defined structure with one single orientation of the two subunits with respect to each other (or two in stereo isomers), and they are not dissociative in the ground state, nevertheless they show a broad structureless fluorescence.

In order to understand this, we must consider the specific properties of the [2.2]phanes. They differ from excimers in so far that the bonds which keep the two subunits together, i.e. the methylene bridges, are different from the excimer-type bonds which are primarily responsible for the spectroscopic properties (neglecting  $\sigma\pi$ -interaction to be discussed below). If we consider e.g. pyrenophane **10**, it is plausible to assume that it behaves analogous to the excimer formed by a pair of pyrene molecules in a single crystal of pyrene, for which Birks [13] calculated a reduction of the distance from 3.53 Å in the ground state to 3.34 Å in the excited state. We make this assumption, namely that in the central part of the phane the distance of 3.65–3.8 Å determined experimentally for the ground state is contracted in the excited singlet state by an excimer type of bonding by a few tenths of an ångström.

We do not attempt at the moment to estimate the degree of contraction quantitatively, but we want to point out that there is an important difference between the [2.2]phanes and the pyrene excimers in single crystals. While in the latter the two subunits are flat discs, their distance from each other being determined by the intersystem excimer-type bonding, the outer ends of the subunits of the phane are forced to a considerably smaller distance by the methylene bridges, but at the same time these bridges like springs force the subunits to bend and hence the central parts away from each other. The equilibrium distance in the excited state is determined by this force and the attracting force of the bonding and there is no doubt that qualitatively it will be smaller than in the ground state without the attracting bonds. Hence one may well speak of a sort of "intramolecular bond dissolution"

in connection with the transition from the first excited singlet state to the ground state, in spite of the fact that the subunits are kept together by the methylene bridges. From the point of view of bonding in this central part of the phane (excluding the atoms to which the methylene bridges are bond and those adjacent to them) the only thing which matters is that the two subunits when emitting a fluorescence light quantum go from an excimer type of bonding to a somewhat larger distance at which we can safely assume that the interaction between the ground state  $\pi$ -orbitals is very close to zero.

In order to clarify this somewhat more we compare the pyrenophane **10** again with a pyrene single crystal. Similar to the situation in the single crystal the two subunits of the phane (pyrene molecules in the crystal) are kept together in the excited state by the excimer-type bonding, they would dissociate in the ground state like excimers in solution if they were not prevented from doing so by the methylene bridges (cage effect in the crystal). An important difference between these cases concerns the energy in excess to the one which is taken by the fluorescence light quantum: In dissociating excimers in solution it is taken up by the kinetic energy of the dissociating monomers, in the pyrene crystal and in the phanes it goes into lattice vibrations of the crystal. Due to the particular structure of the phanes a specific type of vibrations might occur, namely vibrations of the two subunits with respect to each other the frequencies of which we estimate because of the large masses and small forces involved to be rather low. This phenomenon can be described as "intramolecular bond dissolution".

The bent structure of the aromatic subunits of the phanes as distinguished from the pair of flat pyrene molecules in the crystal causes a further important difference between these two. In the latter the distance between the planes is constant and hence the distance between pairs of corresponding C atoms is constant as well. In the phanes, on the other hand, there is a considerable variation in distance in the ground state which is correlated with the rigidity of that distance. If the distance in the central part is larger in the ground state, it can be more contracted in the excited state. Hence those C atoms which possess the highest bond density  $d_{ij}^{\pi}$  and make the predominant contribution to the energy levels (C atoms 1, 3, 6, 8 in pyrenophane **10**) are not necessarily most important for the line-

width as well.

Let us consider the potential energy in the ground state and in the first excited singlet state for the central part of pyrenophane **10** as a function of the distance between the two subunits. It is determined in the ground state by the Born repulsion as well as by the elasticity of the subunits and of the bond angles of the methylene bridges. This results in a rather broad and flat potential well with a large number of narrowly spaced vibrational levels. The potential in the first excited state is determined by the same forces; the main difference is that we must take into account in addition the attractive potential of the excimer-type of bonding which results in a somewhat more marked potential minimum in the excited state. The Franck–Condon transitions from this first excited singlet state into the manifold of the levels in the ground state cause the broad unstructured fluorescence.

### 3.3. The triplet state. Phosphorescence and zero field splitting

We draw our attention now to some properties of the triplet states, such as the red shift and the line-width of the phosphorescence and the reduction of the  $D$  values as compared to the monomers. Both these quantities are large for paracyclophane **6** and much smaller for thephanes with larger distances between the subunits.

(1) Since the distance between the aromatic C atoms varies in the largerphanes from about 2.8 Å to 3.8 Å, we expect from the point of view of distance the highest value of  $P_{ij}$  and hence of  $d_{ij}^{\pi}$  between the  $2p_z$ -atomic orbitals of the carbon atoms which are closest to each other at a distance of about 2.8 Å, i.e. those to which the methylene bridges are linked (which will be termed “bridged” atoms throughout this paper). Our theoretical considerations show that the bond density  $d_{ij}^{\pi}$  is only large if  $F_{ij}$  is large as well, i.e. if they carry a high spin density as the bridged C atoms in dimethylbiphenylene **2** and dimethylfluorene **3** (and hence most probably in the correspondingphanes). However, a strong bond is not formed by the corresponding C atoms 2 and 7 in phenanthrene and pyrene which carry a very low spin density; for these considerations it is not important whether the spin density is accidentally very low as in phenanthreno-

phane or whether the low spin density is a consequence of the symmetry of the system as in pyrenophane where the C atoms 2 and 7 are situated on a nodal plane of the two singly occupied  $\pi$ -orbitals.

Let us discuss next with the example of pyrenophane **10** the interaction in a case where the bond density  $d_{ij}^{\pi}$  between the bridged C atoms 2 and 7 is small because of the low spin density. The next nearest C atoms 1, 3, 6 and 8 carry the highest spin density in dimethylpyrene **5** and we expect those to make the predominant contribution to the bonding between the two subunits. All other C atoms close to the center of pyrenophane **10** are so far apart (3.65–3.80 Å) in the ground state and in the first excited triplet state that we might safely neglect their contribution to the total bond density  $d_{ij}^{\pi}$  in distinction from the behaviour of the excited singlet state discussed above. We attribute this difference which is experimentally borne out by the very small reduction of the  $D$  value and the very small red shift of the phosphorescence as compared to the large red shift of the fluorescence to the farther extension of the excited singlet orbital along the  $z$  direction.

It is very difficult to estimate whether, assuming identical values of  $F_{ij}$ , the sum over two bond densities  $d_{ij}^{\pi}$  between C atoms with a distance of 2.79 Å is larger or the sum over four bond densities  $d_{ij}^{\pi}$  between C atoms with a distance of 3.19 Å. The experimentally observed smaller reduction of the  $D$  values and the smaller red shift in phenanthrenophane **9** and in pyrenophane **10** than in biphenylophane **7** and syn-fluorenophane **8a** seem to indicate that the sum over the two bond densities  $d_{ij}^{\pi}$  at 2.79 Å is considerably larger or, in other words, that  $P_{ij}$  (2.79 Å)  $\gg$   $2P_{ij}$  (3.19 Å), although the  $F_{ij}$  are somewhat higher at the bridged atoms in **7** and **8a** as well.

(2) Phanes which do not have (approximately)  $D_{2h}$  symmetry can form two stereoisomers and an additional effect may occur which we shall discuss with the example of phenanthrenophane **9**. In the syn-form (not included in table I because it could not be obtained in the pure form so far) the same C atoms of the monomers and hence  $2p_z$ -atomic orbitals with identical spin density are always situated opposite to each other in the two subunits as in thephanes which have  $D_{2h}$  symmetry. In the anti-form, however, this is not so. In antiphenanthrenophane **9** the two C atoms 9 and 10 which carry the highest spin density have no

opposite at all in the other subunit; hence we expect  $P_{ij}$  for these C atoms and hence their bond density  $d_{ij}^{\pi}$  to be negligible. The second highest spin density is situated at the C atoms 1 and 8 and the third almost equally high spin density is situated at the C atoms 3 and 6 which are opposite to 1 and 8. Their distance is the second closest in this plane, and we estimate it to be about 3.2 Å in analogy to pyrenophane 10; hence we expect in antiphenanthrenophane 9 a similar situation as in pyrenophane 10, i.e. a predominant contribution of these four atoms to the bond density  $d_{ij}^{\pi}$ . Note, however, that in this case  $i$  and  $j$  refer to C atoms opposite to each other in the plane which are not identical C atoms in the two subunits.

A related but somewhat different situation is encountered in the case of anti fluoreno phane 8b where the X-ray structure analysis [10] shows that the C atoms are not situated directly opposite to each other, fig. 3 in the preceding paper [8]. (The deviation of the "opposite to each other" situation of the C atoms encountered in allphanes, which is due to the somewhat staggered position of the methylene bridges [5,9], is much smaller and is hence neglected here.) Hence none of the  $2p_z$ -atomic orbitals has its direct opposite, they do not point at each other and the result is a considerably reduced bond density  $d_{ij}^{\pi}$ . We expect the predominant contribution to the bond density  $d_{ij}^{\pi}$  in this phane 8b to arise from the "bridged" C atoms 2 and 7 because they are closest to each other (2.79 Å) and carry the highest spin density, while those adjacent to them, which are the second closest, carry a low spin density. The experimental observation, namely the considerably smaller reduction of the  $D$  value and the smaller red shift of the phosphorescence, can be explained by the reduced values of  $P_{ij}$  and hence of the bond density  $d_{ij}^{\pi}$  in the anti fluoreno phane 8b as compared to the syn-fluoreno phane 8a, which is due to the "not opposite to each other" position of the  $2p_z$ -atomic orbitals in the former. In agreement with expectation the experimental results obtained with syn-fluoreno phane 8a are very similar to those found with diphenylo phane 7.

(3) An additional effect which we must take into account is the  $\sigma\pi$ -interaction mentioned above. The  $\sigma\pi$ -interaction of the bonding electrons in the  $\text{CH}_2$ - $\text{CH}_2$ -bridge occurs with the  $2p_z$ -atomic orbital of the "bridged" atoms. Hence we can conclude immediately that this interaction becomes the more important the

higher the spin density is at these atoms, i.e. we expect it to be of little importance for phenanthrenophane 9 and pyrenophane 10, but to be more important for biphenylo phane 7 and the two fluoreno phanes 8a and 8b. We have so far not been able to estimate quantitatively the relative strength of this  $\sigma\pi$ -interaction as compared to the  $\pi\pi$ -interaction between the C atoms to which the bridge is linked. It is clear, however, that this additional  $\sigma\pi$ -interaction increases the contribution of the "bridged" C atoms, as compared to all others, to the total bonding between the two subunits of the phane.

An additional parameter which we must consider in this context is the angle  $\alpha$  between the direction of the  $\text{CH}_2$ - $\text{CH}_2$   $\sigma$ -bond and the symmetry axis of the  $2p_z$ -atomic orbital at the C atom to which the bridge is linked. These two directions are not parallel: because of the bending of the aromatic system the  $2p_z$ -atomic orbital points away from the bridge inside the phane. We define the relevant angle  $\alpha$  to be the angle between the normal to the plane determined by the "bridged" C atom and the two C atoms adjacent to it and the axis of the  $\text{CH}_2$ - $\text{CH}_2$   $\sigma$ -bond. Since this angle  $\alpha = 12.6^\circ$  in paracyclo phane 6 [9], but larger in the largerphanes ( $\alpha_{8b} = 14.2^\circ$  in anti fluoreno phane 8b [10] and  $\alpha_{10} = 16.2^\circ$  in pyrenophane 10 [5]), we expect the  $\sigma\pi$ -interaction, normalized to equal bond densities  $d_{ij}^{\pi}$  in the relevant bond, to be somewhat stronger in paracyclo phane 6 than in the largerphanes, in particular in pyrenophane 10.

(4) We come now to the discussion of the linewidth and the amount of structure observed in the phosphorescence of thephanes. In principle, we attribute the line broadening (as compared to the respective monomers) to the same phenomenon as for the fluorescence discussed above, i.e. to a change in the equilibrium distance in the excited state with respect to the ground state. The main difference between the corresponding excited singlet and triplet orbitals is their extension in space along the  $z$  axis as mentioned above. The difference in behaviour of the fluorescence and phosphorescence and in particular the wide variety of linewidth and structure observed with the latter has its origin in this difference of the size of the orbitals. We have to assume that the excited singlet orbitals extend always so far along the  $z$  direction that the quantity  $P_{ij}$  is finite for all aromatic C atoms in all [2.2]phanes compiled in table 1, and hence there exists an excimer-



type interaction between the two subunits leading to the typical broad and structureless fluorescence. The same is true for the triplet orbitals in the smallest [2.2]paracyclophane **6** with distances between the subunits between 2.79 and 3.10 Å, but not for the largerphanes where  $P_{ij}$  is zero or almost zero for the C atoms close to the center with distances between 3.65–3.80 Å. Therefore we find a great variety of behaviour of the phosphorescence of the largerphanes **7–11** which must be discussed for each phane and for each bond density  $d_{ij}^{\pi}$  separately.

Allphanes have in common the four “bridged” aromatic C atoms with a distance of about 2.8 Å and hence with the highest value of  $P_{ij}$ . Since these C atoms are pressed together by the methylene bridges, it seems highly improbable that their distance undergoes an appreciable additional reduction in the excited state due to the additional bond density  $d_{ij}^{\pi}$ .

If the “bridged” C atoms would contribute appreciably to the linewidth, one would expect taking into account the almost identical  $P_{ij}$  values a correlation with the quantity  $F_{ij}$ .

This is, however, in contrast to the experimental results where we find for the phenanthrenophane **9** with a very low spin density and hence a low value of  $F_{ij}$  a rather large linewidth of the phosphorescence, while the fluorenophanes **8a** and **8b** with a high spin density and a large value of  $F_{ij}$  show a sharp very structural phosphorescence spectrum. We conclude from these theoretical considerations as well as from the experimental results that the contribution of the bridged C atoms to the linewidth of the phosphorescence can be neglected.

We shall now divide all other aromatic C atoms into two groups: Those adjacent to the “bridged” C atoms with typical distances of about 3.1–3.2 Å and all others closer to the center with distances between 3.65–3.80 Å, and we shall discuss the latter first. They have a comparatively higher amount of freedom along the  $z$  axis and can hence undergo a somewhat larger change of distance due to excimer type bonding or due to vibrations of the two subunits with respect to each other. Since  $P_{ij}$  of the excited singlet orbitals is appreciable for all these C atoms and since one or more of them possess in allphanes at least a medium value of  $F_{ij}$ , we have attributed to them the predominant contribution to the line broadening in the fluorescence as discussed above. Because of the lower exten-

sion of the triplet orbitals along the  $z$  direction, however,  $P_{ij}$  vanishes or becomes very small in the first excited triplet state and hence its contribution to the phosphorescence linewidth is also small or zero even for appreciable values of  $F_{ij}$ .

The last type of bonds we must discuss are those of the C atoms adjacent to the “bridged” C atoms. Their distance of about 3.1–3.2 Å is sufficiently close so that we expect the value of  $P_{ij}$  to be appreciable and it is not that rigidly fixed as for the “bridged” C atoms but less mobile than those closer to the center. It is very difficult to estimate which of several small quantities is the relatively largest, but probably the contribution of these C atoms is predominant for the linewidth of the phosphorescence of mostphanes in table I. This would be in quantitative agreement with the sharpest and most structured phosphorescence observed in the fluorenophanes **8a** and **8b**, the  $F_{ij}$  values of which are very low for the atoms 3,3', 5,5' as compared to the somewhat larger linewidth in pyrenophane **10** and the even larger one in phenanthrenophane **9**, the  $F_{ij}$  values of which are fairly large. The difference in linewidth between the last two is, however, not obvious on this basis, neither is the large linewidth observed with biphenylophane **7** which can only be explained when assuming additional degrees of freedom for the internal mobility of this less rigidly built molecule [8].

#### 4. Conclusions

From the considerations discussed in this paper, which are found to be at least in qualitative agreement with the experimental data available at present, we draw the following conclusions:

(1) The crucial quantity for a further understanding of the  $\pi\pi$ -interaction inphanes is the total intersystem charge density (or bond density)  $d_t^{\pi}$ . It is the sum over the bond densities  $d_{ij}^{\pi}$  between the  $2p_z$ -atomic orbitals of the various aromatic C atoms of the two subunits of a phane. The various  $d_{ij}^{\pi} = F_{ij}P_{ij}$  contribute to  $d_t^{\pi}$  appreciably only if both factors of this product are not zero or close to zero.  $P_{ij}$  is essentially a geometric factor which measures the extension of the  $2p_z$ -atomic orbitals in space and their relative position and distance; it vanishes for all pairs of C atoms  $i$  and  $j$  which are not opposite or almost opposite with respect to each other

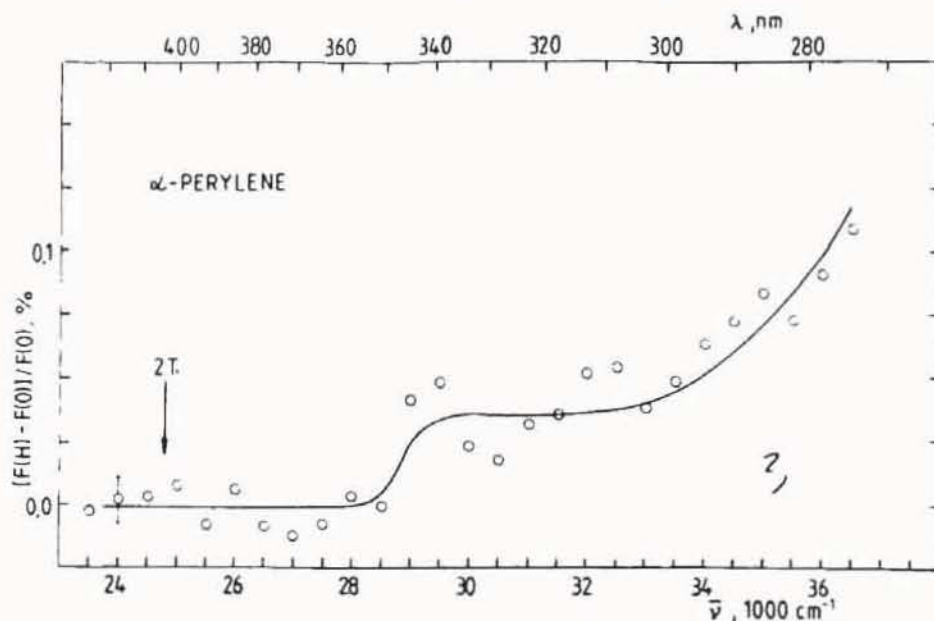


Fig. 3. Excitation spectrum of magnetic field effect on the prompt fluorescence of  $\alpha$ -perylene crystal. Conditions as in fig. 2.

transport properties; e.g. for anthracene crystals  $k_T \approx 10^9 \text{ s}^{-1}$ . The prediction [16] that in  $\alpha$ -perylene fission might not be observable was essentially based on one of the two assumptions: (a) the escape rate  $k_T$  is slow, i.e. the ratio  $k'_T(H)/k_T$  increases, or (b) the fusion rate  $k'_f$  is high when two triplets are formed in adjacent molecules in the very pair, i.e. the ratio  $k_v/k'_f$  decreases. In case they are of any importance at all, neither of the two effects is obviously strong enough to suppress the observation of the fission process in  $\alpha$ -perylene. With respect to the magnitude of  $k_T$ , there has recently accumulated evidence [17] against an excimeric character of the triplet state in pyrene crystals implying similar values of  $k_T$  for monomeric and excimeric crystals.

The special geometry of molecular pairs in  $\alpha$ -perylene might well favour high rates of both,  $k_f$  and  $k'_f$ , i.e. the fine structure parameters of triplets in the  $\alpha$ - and  $\beta$ -crystal might differ from each other. However, a different fine structure cannot be responsible for the drastic change of the excitation spectrum as reflected in the large blue-shift of the threshold for fission. This blue-shift leads to the conclusion that at low excess energies exciton fission in  $\alpha$ -perylene has to compete with a fast relaxation process not occurring in the  $\beta$ -crystal. As such excimer formation in the singlet manifold offers itself. The experiment shows also that at high excess

energies ( $E > 33\,500 \text{ cm}^{-1}$ ) the fission from high electronic states, monomer or excimer, becomes independent of the excimer formation. If this is true, the fine structure parameters of triplets in the two crystal modifications could be similar since we obtain nearly identical fission values for a given orientation of the magnetic field (fig. 1).

A quantitative description of the fission process in excimer forming crystals with respect to competing energy relaxation mechanisms will be given in the next section. The blue-shift observed ( $\approx 3500 \text{ cm}^{-1}$ ) is explained by two relaxation processes, one in the course of excimer formation and a much weaker one occurring in the triplet pair state.

### 3. Dynamics of excimer formation and fission

As pointed out in the introduction, the experimental data can be interpreted if the excimer formation is faster than or comparable to vibrational relaxation, the fission is competing with. Further in this section we will derive the rate of exciton fission from an excimer state and we will show that in  $\alpha$ -perylene the threshold must be higher than in the  $\beta$ -form.

Let us estimate now the time of the excimer formation after the photon absorption in the  $\alpha$ -crystal.

ment is in general not zero and causes the proper wavefunction for large distances between the subunits to be

$$2^{-1/2}({}^3\Psi_3 + {}^3\Psi_4) = 2^{-1/2} \{-|L^\alpha L^\beta R^\alpha r^\alpha| + |R^\alpha R^\beta L^\alpha l^\alpha|\},$$

in which the charge transfer terms are absent.

When for shorter distances between the subunits the degeneracy is removed and the lower of the resulting triplet states gets a higher bonding character and hence a larger coefficient for  ${}^3\Psi_3$  than for  ${}^3\Psi_4$ , we get for this lower triplet state a wavefunction of the type

$$\begin{aligned} {}^3\Psi_A &= \frac{(1+\lambda){}^3\Psi_3 + (1-\lambda){}^3\Psi_4}{[2(1+\lambda^2)]^{1/2}} \\ &= \frac{\{-|L^\alpha L^\beta R^\alpha r^\alpha| + |R^\alpha R^\beta L^\alpha l^\alpha|\}}{[2(1+\lambda^2)]^{1/2}} + \frac{\{-|L^\alpha L^\beta l^\alpha R^\alpha| + |R^\alpha R^\beta r^\alpha L^\alpha|\}}{[2(1+\lambda^2)]^{1/2}}. \end{aligned} \quad (\text{A3})$$

We used the index A to indicate that the total wavefunction is antisymmetric with respect to the plane between the two subunits. With the usual definition for charge density and spin density we find from (A3) that this wavefunction leads to a charge density

$$\frac{3}{2}L^2 + \frac{3}{2}R^2 + \frac{1}{2}l^2 + \frac{1}{2}r^2 - [2\lambda/(1+\lambda^2)](lr + LR) \quad (\text{A4})$$

and to a spin density

$$\frac{1}{2}L^2 + \frac{1}{2}R^2 + \frac{1}{2}l^2 + \frac{1}{2}r^2 - [2\lambda/(1+\lambda^2)](lr - LR). \quad (\text{A5})$$

We assume that the orbitals are orthonormal. It is our experience [24] that in systems of the type considered here one gets two types of orbitals, symmetrical and antisymmetrical ones, with respect to the plane between the subunits and usually degenerate, or nearly degenerate, in case the distance between the subunits is not small. From sum and difference of those orthogonal orbitals one gets orthogonal orbitals which are mainly on the right hand side and mainly on the left hand side, respectively. For the larger interplanar distances these orbitals are approximately equal to the usual  $\pi$ -orbitals for the separate subunits as we assumed in the main text.

If we would have calculated the charge and spin densities for the triplet wavefunctions  $\Psi_1$  and  $\Psi_2$  mentioned in ref. [1], it would have led to a triplet wavefunction which is spatially symmetrical, to be indicated by  ${}^3\Psi_S$ . The expression for the charge and spin density for  ${}^3\Psi_S$  are very similar to the ones for  ${}^3\Psi_A$  and given in (A4) and (A5), the only difference being that for  ${}^3\Psi_S$  in the formula for the charge density a term  $-[2\lambda/(1+\lambda^2)](lr - LR)$  occurs and in the formula for the spin density a term  $-[2\lambda/(1+\lambda^2)](lr + LR)$ .

In monomers and in principle inphanes the value of the spin density at a particular magnetic nucleus is an experimentally accessible quantity through measurement of hyperfine coupling constants. For small values of  $\lambda$  the spin densities are almost completely determined by the first four terms in (A5), half the sum of the squares of the various orbitals. This statement is still true when one has to interpret the hyperfine coupling with a McConnell type of relation obtained by a configuration interaction which is not taken into account in the derivation of (A5). In particular for rather symmetricphanes with two identical subunits of the type of an alternant hydrocarbon, this leads to important information about  $L$ ,  $R$ ,  $l$  and  $r$ . In particular one will be able to predict whether at a certain C atom  $L$ ,  $R$ ,  $l$  or  $r$  have a large value (large coefficient) or is zero or almost zero. Hence knowledge of spin densities can be used to make prediction for the value of  $(lr + LR)$  in the charge density formula as we have done frequently in this paper.

In the main text we assumed that the charge transfer terms were small for the largerphanes, otherwise we would have observed a much larger reduction of the zero field splitting parameter  $D$ , for small  $\lambda$  we approximate  $2\lambda/(1+\lambda^2)$  by  $2\lambda$ . These terms in  $\lambda$  give the major change in charge and spin density between the subunits when we go from a completely decoupled system to an interacting system. It is this term in  $\lambda$  for the charge density (or bond density) which we considered in the main text.

We discuss now briefly the singlet states corresponding to the triplet states. Instead of  ${}^3\Psi_3$  we get then a func-

tion

$${}^1\Psi_3 = (2^{-1/2}/4) \{ |(L-R)^\alpha (L-R)^\beta (L+R)^\alpha (l-r)^\beta| - |(L-R)^\alpha (L-R)^\beta (L+R)^\beta (l-r)^\alpha| \},$$

and a similar expression for  ${}^1\Psi_4$ . When one proceeds with these functions in exactly the same way as we have done above for the triplets, one finally obtains for a singlet function  ${}^1\Psi_A$  an expression for the charge density which is exactly the expression (A4). The spin density is of course zero. For a singlet function  ${}^1\Psi_S$  analogous to  ${}^3\Psi_S$  we get again a change in sign to  $(lr-LR)$ .

Although the expressions for the charge densities are the same for corresponding singlets and triplets, the respective orbitals have usually a different extension in the  $z$ -direction leading to different total intersystem charge densities  $d_i^\pi$  between the subunits.

Besides the formal similarity between singlets and triplets mentioned above, there is, for our discussion, an important difference. The exciton part of the triplet wavefunction is

$$2^{-1/2} \{ |L^\alpha L^\beta R^\alpha r^\alpha| \pm |R^\alpha R^\beta L^\alpha l^\alpha| \}$$

For small interplanar distances the two triplets are not longer degenerate, one of them gets a lower energy than the other and this is mainly responsible for the red shift of the phosphorescence. The matrix element which determines the splitting of the two triplets is

$$\langle |R^\alpha R^\beta L^\alpha l^\beta| H | L^\alpha L^\beta R^\alpha r^\alpha \rangle = -\langle R(1) L(1) | e^2/r_{12} | r(2) l(2) \rangle. \quad (A6)$$

For the corresponding matrix element for the singlet state one finds

$$\begin{aligned} & \frac{1}{2} \langle \{ |R^\alpha R^\beta L^\alpha l^\alpha| - |R^\alpha R^\beta L^\beta l^\alpha| \} H \{ |L^\alpha L^\beta R^\alpha r^\beta| - |L^\alpha L^\beta R^\beta r^\alpha| \} \\ & = 2 \langle R(1) r(1) | e^2/r_{12} | L(2) l(2) \rangle - \langle R(1) L(1) | e^2/r_{12} | r(2) l(2) \rangle. \end{aligned} \quad (A7)$$

The term (A6) vanishes when the overlap  $RL$  and/or  $rl$  vanishes. This happens already at comparatively small distances between the subsystems. The first term in (A7) however does not vanish under these circumstances;  $Rr$  and  $Ll$  are usually not zero and the first integral in (A7) vanishes only for larger distances between the two subsystems. In a zero overlap approximation (A6) becomes zero, this in contrast to (A7), in particular its first integral. (See also ref. [12].) The large red shift of the fluorescence as compared with the smaller red shift of the phosphorescence finds its explanation, in addition to the difference in the extension of the orbitals mentioned above, in the difference between expression (A7) and (A6).

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