TRANSANULAR INTERACTION IN [2.2]PHANES:
[2.2](4,4') DIPHENYLOPHANE AND [2.2](2,7) FLUORENOPHANE

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The emission spectra and the zero field splitting parameters D and E of the first excited triplet states of [2.2](4,4') diphenylophane 3 and of the two stereoisomeric syn- and anti [2.2](2,7) fluorenophanes 4a and 4b are investigated and compared with those of the corresponding monomers. The results are interpreted in terms of the total intersystem bond density d_t^π between the two subunits which is the sum over the bond densities d_{ij}^π between the $2p_z$-atomic orbitals of the various aromatic C atoms i, j of the two subunits ($d_t^\pi = \Sigma_{i,j} d_{ij}^\pi$).

1. Experimental results

In several preceding papers we have studied the transanular π-electron interaction in a number of [2.2] phanes including several isomeric naphthalenophanes, phenanthrenophane and pyrenophane [1–3]. In this paper we report on the emission spectra and the zero field splitting parameters D and E of the first excited triplet states of the monomers 4,4'-dimethyldiphenyl 1 and 2,7-dimethylfluorene 2 as well as on those of the corresponding [2.2] phanes, i.e. [2.2](4,4')-diphenylophane 3 [4] and the two stereoisomeric [2.2](2,7) fluoroenophanes 4a and 4b [5] as shown in table 1 [‡]. These [2.2] phanes have in common that their subunits possess the same π-electron system and the methylene bridges connect the two subunits in analogous positions. For comparison the dimethyl substituted monomers are used since their structure is as close to one half of the corresponding phanes as possible. All measurements were performed in glass matrices at 1.3 K. The experimental set-up used to measure D and E by optical detection of magnetic resonance

Table 1
Phanes and monomers
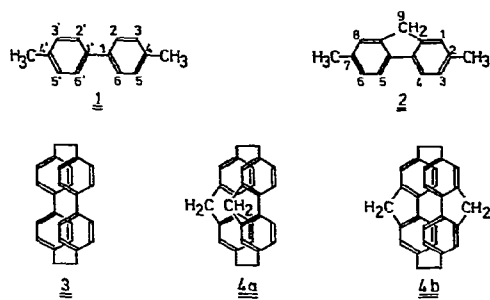
4,4'-dimethyldiphenyl 1, 2,7-dimethylfluorene 2, [2.2](4,4')-diphenylophane 3, [2.2](2,7) fluorenophane (syn) 4a, [2.2](2,7) fluorenophane (anti) 4b. Numbering of atoms in phanes analogous to monomers.

(ODMR) was similar to the one described by Zuclich et al. [6].

The emission spectra of 4,4'-dimethyldiphenyl 1 and of [2.2](4,4') diphenylophane 3 are shown in fig. 1, and in fig. 2 those of 2,7-dimethylfluorene 2 and of the two stereoisomeric [2.2](2,7) fluorenophanes 4a

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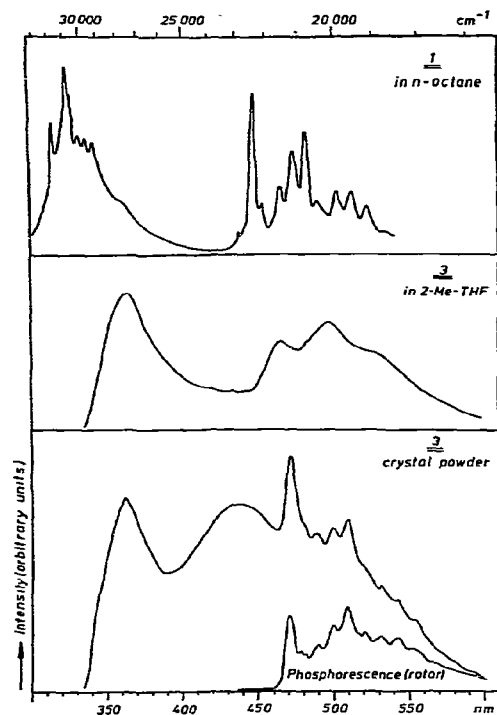[‡] The D and E values and a preliminary emission spectrum of 3 was already included in ref. [1].

Fig. 1. Emission spectra of dimethyldiphenyl 1 and of [2.2] (4,4') diphenylophane 3 in methyltetrahydrofurane and in small neat single crystals at 1.3 K.
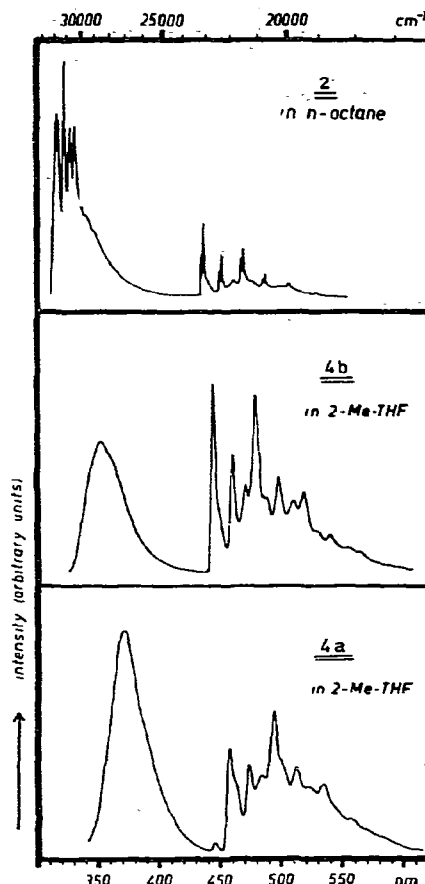
and 4b. The zero field splitting parameters D and E of the excited triplet states of these molecules are listed in table 2 together with the red shift of the fluorescence and of the phosphorescence of the phanes with respect to the corresponding monomers.

Furthermore, we reproduce in fig. 3 the results of an X-ray structure analysis of 4b which has recently been completed [7]. Similar to the results in [2.2] (2,7) pyrenophane [8], the fluorene subunits are bent, the distance between the C atoms to which the bridges are linked is 2.79 Å while the distance between the subunits in the central part is larger. There is, however, an important difference between 4b and [2.2] (2,7) pyrenophane: the two five-membered rings of 4b are approximately planar (except the CH_2-group) and parallel with respect to each other, but because of the anti-position of the two fluorene subunits there are no pairs of C atoms which are directly oppo-

Fig. 2. Emission spectra of dimethylfluorene 2 and of syn-[2.2] (2,7) fluorenophane 4a and the anti-stereoisomer 4b in 2-methyltetrahydrofurane.

site to each other as shown in fig. 3. This has the consequence that the shortest distance between two C atoms in the five-membered rings of the different subunits is 3.82 Å, although the distance between the planes of these rings (3.63 Å) is a little smaller than the distance between the central part in pyrenophane (about 3.80 Å).

2. Discussion

We shall discuss the results in the light of the general

Table 2

Red shifts of emission spectra with respect to monomers and zero field splitting parameters D and E of [2.2](4,4')diphenylophane 3 and the two stereoisomer [2.2](2,7) fluorenophanes 4a and 4b. Parameters D and E of the monomers in cm^{-1}: dimethyldiphenyl 1 $|D| = 0.1070$, $|E| = 0.0055$, dimethylfluorene 2 $|D| = 0.1050$, $|E| = 0.0049$. Uncertainty of shifts due to large linewidth

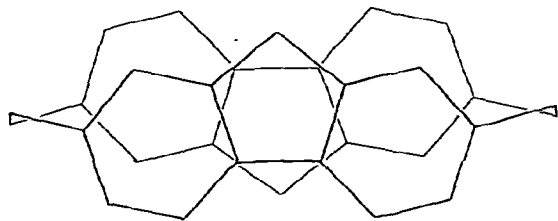| [2.2] phanes	Fluorescence red shift $\tilde{\nu}_{max}^{mon} - \tilde{\nu}_{max}$ (cm^{-1})	Phosphorescence red shift $\tilde{\nu}_0^{mon} - \tilde{\nu}_0$ (cm^{-1})	Zero field splitting parameters		
			$|E|$ (cm^{-1})	$|D|$ (cm^{-1})	$\frac{|D_{mon}| - |D|}{|D_{mon}|}$ (%)
[2.2] (4,4') diphenylophane 3	3200 ± 400	1000 ± 400	0.0030	0.0933	12.8
[2.2] (2,7) fluorenophane (syn) 4a	3900 ± 300	1100 ± 200	0.0032	0.0905	13.8
[2.2] (2,7) fluorenophane (anti) 4b	2600 ± 300	700 ± 200	0.0042	0.0968	7.8

Fig. 3. Projection of anti-[2.2] (2,7) fluorenophane 4b on the plane of the five-membered rings following an X-ray structure determination by Irngartinger et al. [7].

considerations on the relations between spectroscopic properties and structural parameters of [2.2] phanes as outlined in the subsequent paper [9]. It is stated there [9] that the crucial quantity for a further understanding of the $\pi\pi$-interaction in phanes is the total bond density (charge density) $d_t^\pi = \Sigma_{i,j} d_{ij}^\pi$, where d_{ij}^π is the bond density for the bond between C atom i and C atom j in different subunits of the phane. It is further stated that the spin densities ρ_i and ρ_j which are known for the monomers discussed here from measurements of hyperfine coupling constants allow to draw certain conclusions on the bond densities d_{ij}^π if the two identical subunits of the phane are even alternant hydrocarbons, as is the case for the phanes discussed here. For further details and for a justification of the general concept the reader is referred to ref. [9].

Let us begin now with the discussion of the properties of the singlet state, in particular its fluorescence. Its main features are broad structureless bands shifted to the red in agreement with the fluorescence of excimers and of all [2.2] phanes with two identical subunits observed hitherto. These broad bands are attributed in the case of excimers to the dissociation in the ground state. The phanes, on the other hand, possess the specific property that the bonds which keep the two subunits together, i.e. the methylene bridges, are different from the excimer-type bonds between the π-electron systems of the two subunits which are primarily responsible for the spectroscopic properties. In the ground state the distance between the subunits of a phane is entirely determined by the methylene bridges, which force the C atoms to which the bridges are linked together to a considerably smaller distance (2.8 Å) than is encountered in excimers ($\approx$3.5 Å), but at the same time like springs they force the subunits to bend and hence the central parts of the phane to a somewhat larger distance (3.65–3.81 Å). In the excited singlet states, however, there is the additional attractive force of the excimer-type bonds between the π-electron systems of the two subunits and the phanes arrange themselves at an equilibrium distance under the influence of these forces which we estimate to be a few tenth of an ångström smaller than that in the ground state [9]. When a fluorescence light quantum is emitted, this bond is dissolved and the phane returns to the a few tenth of an ångström larger equilibrium distance in the ground state, a phenomenon which we term "intramolecular bond dissolution" [9]. We attribute the broadening of the fluorescence spectra mainly to Franck–Condon transitions from the excited singlet state to the ground state. For a more detailed discussion the reader is referred to ref. [9].

It is difficult to give a quantitative estimation of the red shift of the fluorescence and we do not attempt to do so at the moment. However, the smaller red shift in the anti-[2.2](2,7) fluorenophane **4b** as compared to the syn-isomer **4a** can at least be explained qualitatively by the fact that in the former the various C atoms are not situated in pairs directly opposite to each other as shown in fig. 3 [7]. We shall outline the reasons for this behaviour in some more detail for the analogous situation for the phosphorescence from the triplet state and not here in order to avoid repetition since the arguments are the same.

We come now to the discussion of the properties of the excited triplet states, such as the red shift and the linewidth of the phosphorescence and the zero field splitting parameters D and E as compared to the monomers and we shall begin with the former.

Both monomers carry the highest spin density at the aromatic C atoms to which in the phanes the methylene bridges are linked (which we shall term "bridged" C atoms throughout this paper). Hence we expect these C atoms to have the highest bond density d_{ij}^{π} and to make the predominant contribution to the total bond density d_t^{π}, while for the C atoms adjacent to them (3,5 and 3', 5' in [2.2](4,4') diphenylophane 3 and 1,3 and 6,8 in the [2.2](2,7) fluorenophanes **4a** and **4b**) the spin density and hence the bond density d_{ij}^{π} is very small. The second highest spin density (about half as high as at the bridged C atoms) is found in the monomers at the atoms 2,6 and 2',6' in **3** and the corresponding C atoms in **4a** and **4b**. However, the aromatic subunits of the [2.2] phanes are appreciably bent and, although the X-ray structure determination of **3** and **4a** is not yet completed, we extrapolate from analogy with [2.2](2,7) pyrenophane [8] and **4b** that the distance varies from about 2.8 Å for the "bridged" C atoms in different subunits to about 3.65 Å to 3.8 Å for the C atoms in the center part of the phane.

Another conclusion drawn in ref. [9] is that the excited triplet $2p_z$-atomic orbitals extend less in space along the z direction than the singlet orbitals. Because of the smaller extension of the orbitals, we expect the values of the bond density d_{ij}^{π} in the center between pairs of C atoms in the two subunits to be very small in the excited triplet state in contrast to the excited singlet states where these d_{ij}^{π} values make a larger contribution to d_t^{π}. Since d_{ij}^{π} at the "bridged" C atoms

does not contribute appreciably to the linewidth because these atoms are so strongly pressed together by the methylene bridges and hence their distance is so fixed that the change between the ground state and the first excited state must be very small [9], we expect those near the center to be mainly responsible for the large linewidth of the fluorescence in the phanes discussed here. The much sharper lines of the phosphorescence are explained within this framework by the shorter extension of the excited triplet $2p_z$-atomic orbitals along the z direction which prevent an excimer-type of interaction in the [2.2] phane.

The broad phosphorescence bands observed with [2.2](4,4') diphenylophane **3**, however, cannot be explained on this basis. We have included in fig. 1 for comparison the emission spectrum of small neat single crystals of **3** which shows a well resolved vibrational structure in contrast to the same spectrum in a glass matrix. The cause of the line broadening could be the less rigid structure of the subunits (4,4'-dimethyl-diphenyl **1**) which permit torsional vibrations around the long axis in both subunits of **3**. If this is true, the difference between the spectra in a glass matrix and in neat single crystals could be explained by the higher degree of steric hindrance of such vibrations in the more rigidly fixed single crystal as compared to the glass matrix. An alternative explanation, namely a specific interaction with the glass matrix, seems to be less probable since we found essentially the same broad emission spectra in different glasses (n-octane, 2-methyltetrahydrofurane and polymethylmethacrylate).

The red shift of the phosphorescence of anti-[2.2](2,7) fluorenophane **4b** is somewhat less than for the syn-isomer **4a**. We believe that this smaller red shift is due to the same cause as the even more marked difference in the reduction of the D value (almost a factor two, see table 2) and we shall explain it together.

When discussing D and E we should keep in mind that they measure the dipole–dipole interaction between the two triplet electrons and consequently they decrease with increasing average distance between these electrons. Their reduction with respect to the corresponding monomers depends on the total intersystem charge density d_t^{π}; i.e., the higher d_t^{π} is, the more we expect the D value of a phane to be reduced with respect to the corresponding monomer [9].

In general, the reduction of D in the [2.2] phanes

with two identical subunits discussed here is rather small as shown in table 2 indicating that the two triplet electrons have a high probability of being at a given time in the same subunit of the [2.2] phane. **3** and **4a** possess a similar π-electron system and the two subunits are in both [2.2] phanes situated directly opposite to each other. Hence we are not surprised to find a similar reduction of the D value.

A somewhat different situation, however, is encountered in the case of the anti-[2.2](2,7) fluorenophane **4b**. In fig. 3 the result of an X-ray structure determination [7] is reproduced in the form of a projection on the planes of the subunits. It shows that the various C atoms are not situated in pairs directly opposite with respect to each other, but in a position where none of the $2p_z$-atomic orbitals has its direct opposite. That means that they do not point at each other and the result is a considerably reduced total bond density d_t^π.

The predominant contribution to the bond density d_t^π in **4b** arises from the "bridged" C atoms 2 and 7 because these are closest to each other (2.79 Å) and carry the highest spin density, while those adjacent to them (1, 3, 6, 8) which are the second closest (about 3.2 Å) carry a very low spin density. However, since the "bridged" C atoms are fixed or almost fixed in space, they do not contribute to the extra Franck—Condon type of coupling mentioned above; therefore the phosphorescence of the syn- and anti-isomers **4a** and **4b** is so sharp and structured.

The smaller D value reduction and the smaller red shift of the phosphorescence can be explained by the reduced values of the total bond density d_t^π, in particular the bond density d_{ij}^π of the "bridged" C atoms in the anti-isomer **4b** as compared to the syn-isomer **4a** due to the fact that in the former the various $2p_z$-atomic orbitals in the two subunits do not point pairwise at each other.

It should be noted that the $\sigma\pi$-interaction [10] with the CH_2-CH_2-bonds discussed in ref. [9] is expected to play an important role in the three phanes discussed here because this interaction occurs with

the $2p_z$-atomic orbitals at the "bridged" C atoms which have the highest bond density d_{ij}^π in these phanes. This must remain a qualitative argument for the time being, since the relative strength of this $\sigma\pi$-interaction as compared to the $\pi\pi$-interaction between the two subunits has not been calculated so far.

3. Conclusions

The main conclusion of this paper is that the spectroscopic data, i.e. the red shifts and the linewidth of the emission spectra and the reduction of the zero field splitting parameters D and E with respect to the corresponding monomers of the [2.2] phanes **3**, **4a** and **4b** investigated here, can be interpreted in terms of the total intersystem bond density d_t^π between the two subunits which is the sum over the bond densities d_{ij}^π between the $2p_z$-atomic orbitals of the various aromatic C atoms of the two subunits. For a more detailed discussion the reader is referred to the subsequent theoretical paper.

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