

OPTICAL DETECTION OF MAGNETIC  
RESONANCE (ODMR) OF NAPHTHALENOPHANES

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Investigations of the transannular  $\pi$ -electron interaction in [2.2]-naphthalenophanes [1] by ODMR in zero field were extended to a number of [3.3] naphthalenophanes (1-4, fig 1). Table 1 shows the triplet zero field splitting parameters D and E for 1-4 together with those of the chiral (5)- and achiral [2.2](2,6) naphthalenophane (6) and the monomer 2,6-dimethylnaphthalene (7). All measurements were done in low concentration ( $\sim 10^{-3}$  M) in methylcyclohexan at 1.3K.

Fig. 1

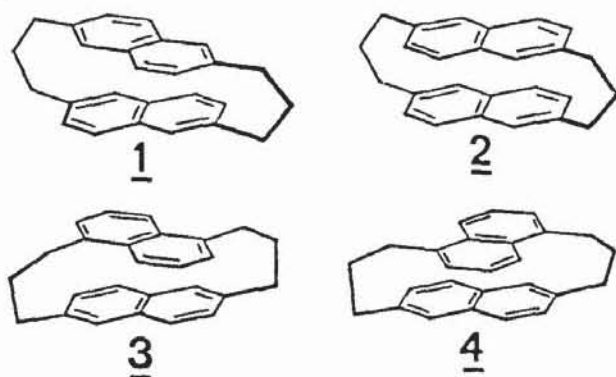


Table 1 ZFS-Parameters

	$ D $ [ $\text{cm}^{-1}$ ]	$ E $ [ $\text{cm}^{-1}$ ]
1	0.0854	0.0194
2	0.0654	0.0168
3	0.0885	0.0147
4	0.0824	0.0130
5	0.0394	0.0154
6	0.0689	0.0128
7	0.0970	0.0155

From the comparison of the D and E parameters as well as from the fluorescence- and phosphorescence redshifts [2] for 1,2 and 5,6 with respect to the monomer 7 it can be concluded that for the [3.3]phanes 1 and 2 a stronger  $\pi$ -electron interaction through space exists. The deviation from planarity for the naphthalene units observed usually is smaller in the [3.3]phanes 1 and 2 than in the [2.2]phanes 5 and 6 [3].

Therefore the transannular distance at the positions 1,4,5,8 between the two naphthalene subunits should be smaller in 1 and 2 than in 5 and 6 [3]. This results in a stronger  $\pi$ -electron interaction for 1, 2 as compared to 5,6 in agreement with the experimental finding, because these positions carry the highest spin densities [4] and hence the highest bond densities  $d_{ij}^{\pi}$  [5]. In contrast the somewhat larger transannular distance in the 2,6 positions should have a minor effect due to the small spin densities. For a geometrical arrangement of the naphthalene subunits similar as in 4 a stronger excimer-type bond in the triplet state is predicted from SCF-LCAO calculations [6] than in 2. Actually a second maximum in the strength of the  $\pi$ -electron interaction can be observed for 4 as can be seen from a comparison of the fluorescence- and phosphorescence redshifts as well as of the reductions of the D parameters of 1,2,3,4 with respect to the monomer 7, but in allphanes studied the strongest  $\pi$ -electron interaction was always observed in the mirror symmetric sandwich arrangement as in 2. In this orientation the maximum intersystem bond density  $d_t^{\pi}$  [5] is expected as well.

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