ODMR OF PHANES AND CHARGE TRANSFER PHANES

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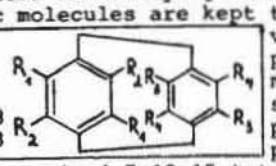
Abstract: Triplet zero field splitting parameters |D| and |E| and decay rates k_i of the triplet sublevels of two stereoisomeric tetramethoxy[2.2]paracyclophanes as well as those of two CT[2.2]paracyclophanes in low concentration in glasses and in small neat single crystals as measured by ODMR in zero field at 1.3 K are presented.

Introduction: The physical properties of dimers, excimers and charge transfer complexes depend to a large extent on the interaction between the π-electron systems through space. Suitable systems for studying such transanular interactions are phanes in which two planar aromatic molecules are kept together by methylene bridges. In several preceding papers [1,3] we reported our studies on [2.2]phanes with more than one aromatic ring per subunit such as naphthalenophanes, fluorenophanes, phenanthrenophanes, diphenylophane and pyrenophane. Here we report ODMR results of two stereoisomeric 4,7,12,15-tetramethoxy[2.2]paracyclophanes (see Fig) the pseudo-ortho compound (3) and the pseudo-geminal compound (4) as well as of two CT-[2.2]paracyclophanes, the pseudo-ortho (5) and the pseudo-geminal 4,7-dicyano 12,15-dimethoxy[2.2]paracyclophane (6) (Fig.) in low concentration in glasses and in small neat single crystals. The emission spectra of 3, 4, 5 and 6 and part of the zero field splitting parameters were reported elsewhere [4,5].

3: $R_1 = R_4 = OCH_3$, $R_2 = R_3 = H$
4: $R_1 = R_3 = OCH_3$, $R_2 = R_4 = H$
5: $R_1 = CN$, $R_2 = R_3 = H$, $R_4 = OCH_3$
6: $R_1 = CN$, $R_2 = R_4 = H$, $R_3 = OCH_3$



Results: are shown in the Table. For 5 and 6 in glasses it was not possible to measure the individual decay rates k_i because of very weak phosphorescence emission. A still lower phosphorescence intensity was found when studying a similar pair of CT-phanes, namely the pseudo-ortho (7) and the pseudo-geminal (8) 4,7-dicarbomethoxy 12,15-dimethoxy[2.2]paracyclophane. We found for 7 in glasses: |D| = 0.0646 cm^{-1}, |E| = 0.0142 cm^{-1} and crystals: |D| = 0.0267 cm^{-1}, |E| = 0.0062 cm^{-1} and for 8 in glasses: |D| = 0.0356 cm^{-1} |E| = 0.0082 cm^{-1} and in crystals: |D| = 0.0225 cm^{-1}, |E| = 0.0018 cm^{-1}.

	in glasses 1	2	in glasses 3	4	single cryst. 3	4	in glasses 5	6	single cryst. 5	6
|D| [cm^{-1}]	0.1216	0.1143	0.0983	0.0901	0.1001	0.0846	0.0642	0.0313	0.0259	0.0231
|E| [cm^{-1}]	0.0222	0.0351	0.0287	0.0226	0.0279	0.0248	0.0150	0.0049	0.0076	0.0043
k_x [sec^{-1}]	0.37	0.11	0.83	5.5	0.53	5.0	-	-	35.1	310
k_y [sec^{-1}]	1.33	0.67	5.3	6.7	3.6	7.7	-	-	3.2	9.1
k_z [sec^{-1}]	0.11	0.16	3.3	1.8	2.0	1.3	-	-	14.3	123
k_{av} [sec^{-1}]	0.60	0.31	3.14	4.67	2.04	4.67	4.26	10.5	17.5	147.4

Table: Zero field splitting parameters |D| and |E|, decay rate constants k_i and average decay rate constants $k_{av} = 1/3 \sum k_i$ of the [2.2]phanes 3 to 6 in low concentration in glasses (MTHF) and in small neat single crystals as well as those of the corresponding monomers 1 and 2. 1 = 1,4-dimethyl 2,5-dicyanobenzene, 2 = 1,4-dimethyl 2,5-dimethoxybenzene, 3 = pseudo-ortho 4,7,12,15-tetramethoxy[2.2]paracyclophane, 4 = pseudo-geminal-4,7,12,15-tetramethoxy[2.2]paracyclophane, 5 = pseudo-ortho 4,7-dicyano 12,15-dimethoxy-[2.2]paracyclophane, 6 = pseudo-geminal 4,7-dicyano 12,15-dimethoxy[2.2]paracyclophane.

Discussion: The reductions of |D| and |E| in the phanes with respect to the corresponding monomers are correlated with the red shifts of the fluorescence and phosphorescence [4,5]. The decay rates k_i and the average decay rate k_{av} show an analogous behaviour. The decay rates of the phanes with two identical subunits are typically one order of magnitude larger than those of the monomers while those of the CT-phanes are still larger up to more than two orders of magnitude as compared to the corresponding monomers. Furthermore, k_i and k_{av} depend strongly on the orientation of the subunits with respect to each other; the decay rate constants of the pseudo-geminal phane which possesses a stronger transanular π-interaction is considerably larger than the one of the corresponding pseudo-ortho phane. Hence we conclude that the decay rate constants k_i and k_{av} are suitable parameters to discriminate between different isomeric [2.2]phanes as well as between the phanes and the corresponding monomers. A very similar behaviour was observed for the triplet state of electron donor-acceptor complexes [6].

References: [1] D. Schweitzer, J.P. Colpa, J. Behnke, K.H. Hausser, M. Haenel and H.A. Staab, Chem. Phys. 11 (1975) 373. [2] D. Schweitzer, K.H. Hausser, R.G.H. Kirrstetter and H.A. Staab, Z. Naturforsch. 31a (1976) 1189. [3] J.P. Colpa, K.H. Hausser and D. Schweitzer, Chem. Phys. 29 (1978) 187. [4] W. Goldacker, K.H. Hausser, D. Schweitzer and H.A. Staab, J. Luminscence, in print. [5] D. Schweitzer, K.H. Hausser, V. Taglieber and H.A. Staab, Chem. Phys. 14 (1976) 363. [6] M. Yagi, N. Nishi, M. Kinoshita and S. Nagakura, Molecular Physics 35 (1978) 1369.