ODMR OF TRIPLET STATES OF ORGANIC ELECTRON DONORS.

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ABSTRACT: Energies of the first excited triplet states and triplet zero
field splitting parameters /D/ and /E/ of several organic donors - usually
used for the preparation of organic metals and superconductors - are
reported.

1. INTRODUCTION

Organic metals and superconductors have caused considerable in­
terest during the last years. Especially molecules of the TTF-family as
well as simple aromatic hydrocarbons like perylene are very promising
electron donors in order to prepare new highly conducting organic metals
or even superconductors. For the preparation of such conducting charge
transfer complexes or radical salts the electronic ground state and ex­
cited state properties of these molecules are of principle interest, but
very little is known about the electronic properties of the excited
electronic states of most of those donors.

Here we report investigations of the first excited triplet state of the
donors perylene (PE)1, tetraphiafulvalene (TTF)2, 4.5-ethylenedithiol­
1.3-dithiolo-2-thione (EDT)3, bis (4.5-ethylenedithio)tetra­thiaful­
valene (BEDT-TTF)4 and 4.5-dimethyl-4'.5'ethylenedithio-tetra­thia­
fulvalene (DIMET)5.

2. RESULTS

Table one shows the energies of the first excited triplet states and
the triplet zero field splitting parameters /D/ and /E/ as obtained
by optical detection of magnetic resonance (ODMR) of the organic donors 1 - 5 at 1.3 K. In the case of perylene1 the results were obtained from
neat single crystals, because perylene does not show phosphorescence
emission neither by S0–S1, nor by direct S0–T1 excitation. Therefore a
delayed fluorescence method (DF-ODMR) after direct S0–T1 excitation
was used. Only two DF-ODMR-transitions at 1.559 and 1.718 GHz could be
observed. The results of the sulphur-donors 2-5 were obtained from low
concentration solutions (n-octane or tetrahydrofurane) frozen to glasses
in order to keep intermolecular interactions small. In the case of
EDT (3) the /D/ and /E/ values result from neat polycrystalline materi­
al, because in glasses no ODMR-transitions could be observed. Due to
the heavy atom effect the donors 2-5 show strong phosphorescence emis­
sions.
Tab. 1 Energies of the first excited triplet state $T_1$ and triplet zero field splitting parameters of donors 1 - 5.

3. DISCUSSION

The energy of the first excited triplet state of perylene 1 is with $12376 \text{ cm}^{-1}$ relatively low. This results in a non radiative desactivation (energy gap law) and a short lifetime (<1 msec.) of the triplet state. The two observed OF-ODMR transitions correspond to two possible D-values ($0.0546 \text{ cm}^{-1}$ or $0.0835 \text{ cm}^{-1}$). MO-calculations of the zero field splitting parameters of perylene gave a D-value of $0.072 \text{ cm}^{-1}$ respectively $0.077 \text{ cm}^{-1}$ (ref. 2 and 3). Therefore we conclude that the two observed OF-ODMR-signals correspond to the $2/E_1$ and $/D/-/E_1$ transitions. This results in a D-value of $0.0835 \text{ cm}^{-1}$, a typical value for a hydrocarbon of this size.

The energies of the triplet state of the sulphur donors 2-5 are about $5000 \text{ cm}^{-1}$ higher with respect to the triplet state of perylene. The triplet zero field splitting parameters $|D|$ of 2-5 are of a similar size as one would expect them from corresponding pure hydrocarbons. This shows that in the case of 2-5 the zero field splitting parameters can be described mainly by contributions of a magnetic dipol-dipol-interaction between the triplet electrons and are only little effected by contributions due to a heavy atom effect.

REFERENCES

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