

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 interest 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 excited 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, tetrathiafulvalene (TTF)2, 4.5-ethylenedithiolo-1.3-dithiolo-2-thione (EDT)3; bis (4.5-ethylenedithiolo)tetrathiafulvalene (BEDT-TTF)4 and 4.5-dimethyl-4'.5'-ethylenedithiolo-tetrathiafulvalene (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 perylene 1 the results were obtained from neat single crystals, because perylene does not show phosphorescence emission neither by S_0-S_1 , nor by direct S_0-T_1 excitation. Therefore a delayed fluorescence method (DF-ODMR) after direct S_0-T_1 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 tetrahydrofuran) 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 material, because in glasses no ODMR-transitions could be observed. Due to the heavy atom effect the donors 2-5 show strong phosphorescence emissions.

substance	T_1 (cm ⁻¹)	D (cm ⁻¹)	E (cm ⁻¹)
PE <u>1</u>	12376	0.0835	0.026
TTF <u>2</u>	17240	0.142	0.028
EDT <u>3</u>	18200	0.167	0.0315
BEDT-TTF <u>4</u>	16600	0.134	0.0174
DIMET <u>5</u>	16810	0.140	0.016

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 cm⁻¹ relatively low. This results in a non radiative deactivation (energy gap law) and a short lifetime (<1 msec.) of the triplet state. The two observed DF-ODMR transitions correspond to two possible D-values (0.0546 cm⁻¹ or 0.0835 cm⁻¹). MO-calculations of the zero field splitting parameters of perylene gave a D-value of 0.072 cm⁻¹ respectively 0.077 cm⁻¹ (ref. 2 and 3). Therefore we conclude that the two observed DF-ODMR-signals correspond to the 2/E/ and /D/-/E/ transitions. This results in a D-value of 0.0836 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 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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