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Charge Transfer descriptors application: TD-DFT protocol for analysis on DMABN transitions and push-pull effect on D-π-A dyes.

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INTRODUCTION

Charge transfer (CT) involving excited state is a phenomenon that arouses the interest of different research groups, not only because it is useful for the development of electronic devices and solar cells, but also because quantifying the magnitude of this effect is still a challenge. The great interest in this phenomenon moves the scientific community towards the development of ways to identify the different types of electronic transitions and, in particular, quantify transitions with charge transfer character.

In this sense, this work aimed the comparison of three descriptive tools, Δr, D_{CT} and Φs, based on TD-DFT calculations, to study the character of electronic transitions. To evaluate the performance of these charge-transfer descriptors, we adopted two aspects: sensitivity against geometries changes and solvent effect, and donor/acceptor group strength in D-π-A (Donor-π bridge-Acceptor) molecules. For the first study, we used the molecule 4-(dimethyl amino) benzonitrile (DMABN) (Figure 1-a), as a model, since it is a well-known example of a molecule that presents state inversion with dimethylamine rotation, and electronic excitations of determined character. For the second study, we applied in a series of push-pull molecules, some recently synthetized, characterized by our group (Figure 1-b) and a third part, similar to those proposed as a new structure, in order to check if the descriptors can describe properly the character of the main electronic transitions, according to the increase in the push-pull effect.

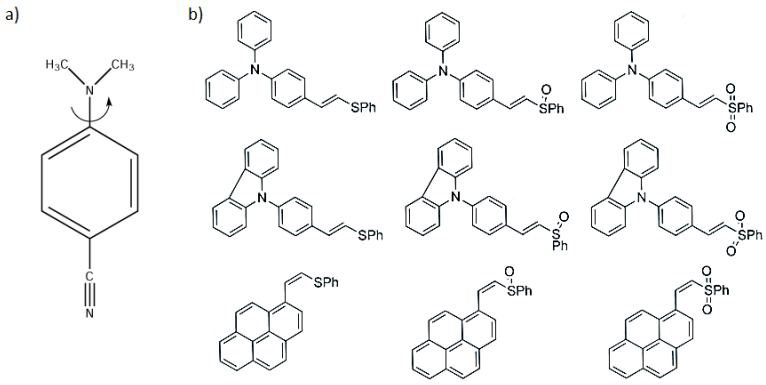

Figure 1: a)DMABN structure b)D-π-A dyes structures

METHODOLOGY

Time-Dependent Density Functional Theory (TD-DFT) calculations were carried out at CAM-B3LYP/cc-pVDZ level for geometry optimization and CAM-B3LYP/jun-cc-pVTZ level for the transition analysis in gas phase and acetonitrile (using Polarizable Continuum Model). Descriptors analyses were carried out with proper software: MULTIWFN for Δr and D_{CT}, and NancyEx for Φs.

RESULTS AND DISCUSSION

The analysis with D-π-A dyes aimed at the validation in the influence of the donor/acceptor group for the constitution of the push-pull effect strength. Variations of the donor group (from pyrene to triphenylamine and later to carbazole) and of the acceptor group (from sulfide to sulfoxide and later to sulfones), showed great increase in the charge transfer character, which have been described in a satisfactorily way with all descriptors.

The analysis with DMABN molecule aimed at the evaluation of the descriptors, against changes of conformation and addition of solvent. The overall performance for the conformation changes were satisfactorily, however, regarding the addition of the solvent effect (acetonitrile), Φ_S descriptor presented difficulties to describe the S_1/S_2 inversion, a characteristic well known of DMABN, most likely because of the theoretical approach used.

As an overall analysis, D_{CT} index present in its analysis a goroup of auxiliary quantitative indexes that can be of great help when considering charge-transfer related properties. In particular, q_{CT}, which is an indication of the amount of charge that has been transferred should be considered as the great differential of this index.

CONCLUSIONS

The objective has been fully accomplished by D_{CT} and Δr descriptors. Both have presented results consistent with the proposed changes. Φ_S showed difficulties in describing the solvent effect, which is crucial for understanding DMABN states behavior and important for material applications. It has been shown that charge transfer description tools can be an efficient way in determining the character of electronic transitions. As a strong charge-transfer character is of extreme importance for technological applications, the use of descriptor tools along with calculations, for research groups aiming the development of efficient D-π-A dye-based materials, should be encouraged.

Keywords: **TD-DFT, DSSC, DMABN, charge-transfer**

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