

Application of DFT Calculations in Designing Naphthalimide- π -Dimethylanilines

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Abstract

The introduction of density functional theory (DFT) has tremendously aided the application of computational material science in the design and development of organic materials. The use of DFT and other computational approaches avoids time-consuming empirical processes. Therefore, this review explored how the DFT computation may be utilized to explain some of the features of organic systems. First, we went through the key aspects of DFT and provided some context. Then we looked at the essential characteristics of an organic system that DFT simulations could predict. Gaussian software had been employed with the B3LYP functional and 6-31G(d, p) basic sets for organic systems.

Keywords

DFT, organic materials, B3LYP, 6-31G(d, p) basic sets

1. Introduction

Computational methodologies, such as density functional theory (DFT), have been developed to bypass time-consuming empirical procedures for the optimization of these formulations [1,2].

DFT computations, in particular, offer outstanding levels of accuracy with comparable computation time and are more inexpensive in terms of computational resources than other ab initio approaches currently in use. Additionally, it avoids the many electron wave function in favor of electron density, and has the potential benefit of dealing with only one function of a single spatial coordinate. Moreover, it employs generalized gradient approximations (GGAs), which use the density gradient to generate a more precise function [3].

DFT are a strong and low-cost method for revealing a material's fundamental information, including energy, geometric structure, electrical, and optical characteristics. It offers important theoretical predictions and assistance from the standpoint of material design. It provides crucial information at the levels of atoms, molecules, and unit cells from the perspective of interpreting the results. The influence of element doping on the geometric and electrical characteristics of organic compounds carriers, as well as the interaction between the molecules and the nanocarriers, is considerably aided by DFT calculations [4].

2. Experimental section

Computational details

Quantum chemical calculations of studied derivatives were performed using DFT and TD-DFT implemented in the Gaussian 16 [5] software package. Geometry optimization was provided by means of density functional CAM-B3LYP method and 6-31g(d,p) basis set in the ground S0 state as well as the lowest excited S1 state. Solvent surrounding (cyclohexane, acetonitrile) was simulated using PCM method. The evaluation of the twisted excited states was carried on with semi-empirical MOPAC, using PM7 Hamiltonian, including solvent with COSMO model [6].

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3. Results and discussion

DFT modelling, intramolecular charge transfer

Optimized ground state geometries and charge density distributions in HOMO and LUMO states of compounds NA1 and NA2 in cyclohexane (CyHex) are depicted in Figure 1. Both molecules reveal a CT nature of electronic transition. The HOMO state comprises charge redistribution between NI and DMA moieties, while the charge density in the LUMO state is localized mainly on NI core. The studied compounds show different twist angles between NI and DMA moieties. Compound NA1 with phenyl ring as a π -linker has a pre-twisted geometry in a ground state: the twist angle between dimethylamine and benzene (ϕ_1) is 9° , while between NI and DMA (ϕ_2) is 51° .

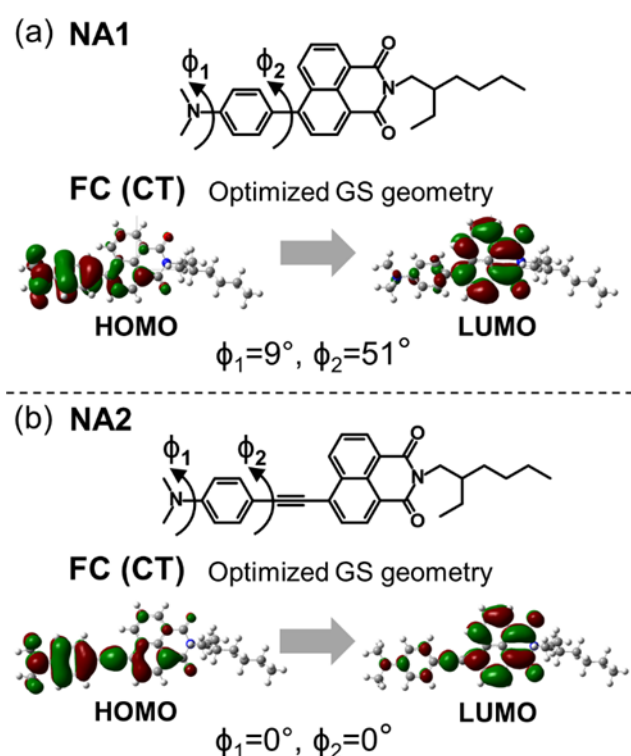


Figure 1. Molecular structures and optimized ground state geometries with calculated electron density distributions for HOMO and LUMO molecular orbitals of compounds NA1 (a) and NA2 (b) in cyclohexane. Here 0° angle denotes planar configuration.

Compound NA2 with phenyl-acetylene junction possess a planar ground state geometry. No ground state geometry changes were noted in solvents of higher dielectric constant (Table 1). The energies of upwards transitions of singlets states as well as a short comment on the excited state optimization are provided in Table 2.

Table 1. Calculated dihedral angles in the ground and excited state geometries of NA1 and NA2 and energies of electronic transitions $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ in different solvents.

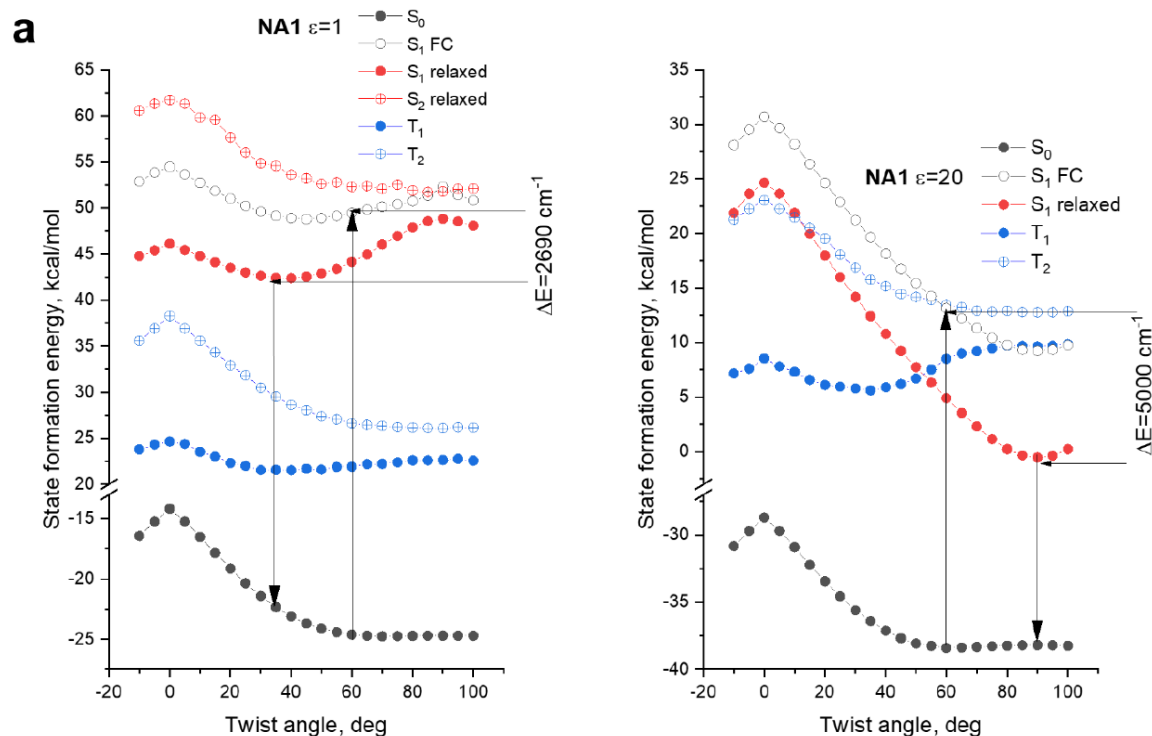
Compound	Solvent	Ground state		Excited state		$S_0 \rightarrow S_1$,	$S_1 \rightarrow S_0$,
		ϕ_1^1	ϕ_2^2	ϕ_1^3	ϕ_2^3	eV	eV
NA1	CyHex	7.32	53.14	0.2	33.97	3.48	2.87
	ACN	7.35	51.88	0.97	31.51	3.35	2.57
NA2	CyHex	1.33	0.92	0.74	0.48	3.15	2.69
	ACN	0.16	0.43	0.25	0.49	3.07	2.38

1 ϕ_1 denotes angle between dimethylamine and benzene ring.

2 ϕ_2 denotes angle between naphthalimide unite and benzene ring.

3 Angles between dimethylamine and benzene ring (ϕ_1) and between naphthalimide unit and benzene ring (ϕ_2) in the excited state geometry. For the comment on the obtained values, see text below Table 1.

The optimisation of the potential surface of the lowest excited singlet when varying the twist angle was not successful with selected long-range separated functional CAMB3LYP and PCM solvent model, i.e., no significant twist was obtained in acetonitrile and the calculated transition energies ($S_1 \rightarrow S_0$) reassembles only the blue fluorescence spectra band. On the other hand, the semi-empirical evaluation with PM7 Hamiltonian of MOPAC (with solvent model COSMO) allowed to reproduce the twisted geometries of NI compounds in most polar environment, as showed in Figure 2.



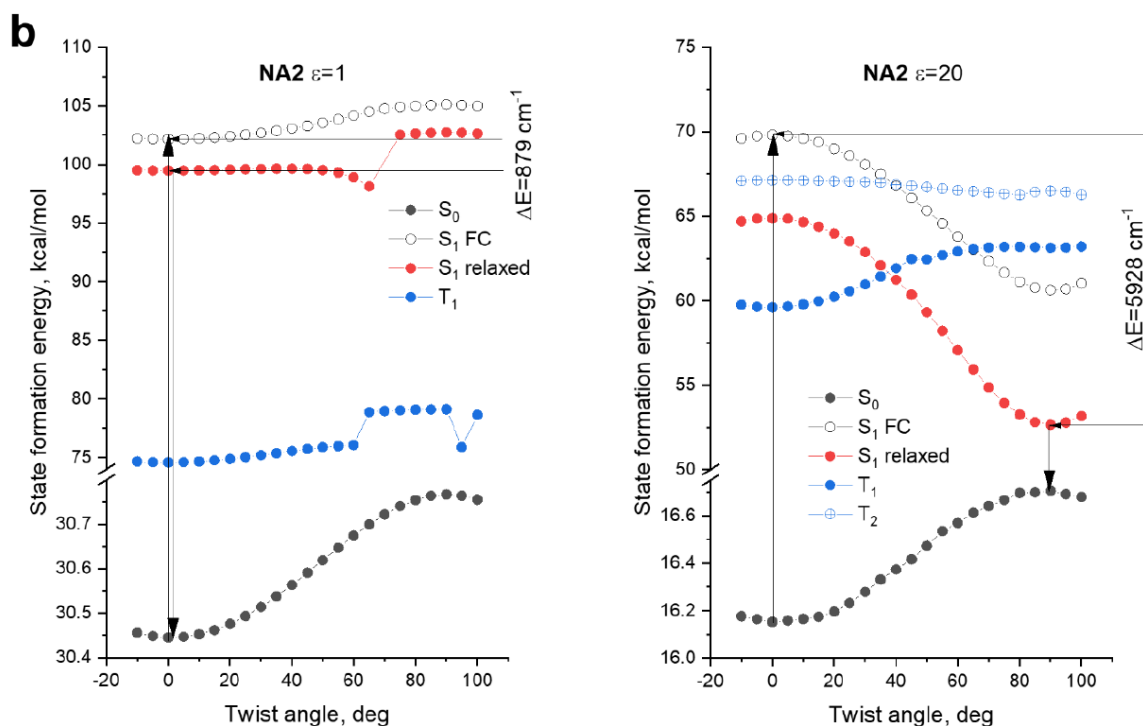


Figure 2. Potential energy surfaces versus twist angle between naphthalimide unit and dimethylaniline for NA1 (a) and NA2 (b) in non-polar (with $\epsilon=1$) and polar (with $\epsilon=20$) environments, obtained with semi-empirical method (PM7 Hamiltonian of MOPAC, solvent model COSMO).

Table 2. The calculated ground state dipole moments.

Compound	Solvent	μ , D
NA1	CyHex	8.5
	ACN	9.6
NA2	CyHex	11.3
	ACN	9.9

4. Conclusions

Two new twisted intramolecular charge transfer (TICT) donor- π -acceptor compounds were designed by combining a well-known electron acceptor naphthalimide unit with a classic electron donor dimethylaniline through two types of different rigid linkers. The increase of solvent polarity determines the competition between CT and TICT states. The pre-twisted geometry of compound has no influence in terms of excited state reaction rates. On the other hand, the higher difference between ground and excited state dipole moments determines faster excited state processes.

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