



Computational Molecular Nanoscience: A Study of the Molecular Structure and Properties of a RAFT Polymerization Agent

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Abstract

In this work, we make use of a model chemistry within Density Functional Theory (DFT) recently presented, which is called M05-2X, to calculate the molecular structure of dibenzyl trithiocarbonate (DBTTC), as well to predict its infrared (IR) and ultraviolet (UV-Vis) spectra, the dipole moment and electrical polarizability and static first hyperpolarizability.

Keywords: Molecular structure, infrared spectrum, ultraviolet spectrum, dipole moment, polarizability, RAFT polymerization agent.

Introduction

RAFT polymerization has recently emerged as a promising controlled radical polymerization due to its operation simplicity and the resultant polymers free from the contamination of metal catalyst¹. The objective of this work is to report the results of the calculation of the molecular structure and properties of one of the most common RAFT polymerization agents, dibenzyl trithiocarbonate (DBTTC)² using a recently developed density functional³.

Material and Methods

For what concerns the calculation of the gas phase terms, we have chosen the hybrid meta-GGA M05-2X functional³, which consistently provides satisfactory results for several structural and thermodynamic properties. The presence of anionic species makes the use of diffusion functions mandatory⁴ and for the sake of consistence, we have used the same basis set for all the computations. As a consequence we selected the G-31+G(d,p) basis set for geometry optimizations and evaluations of harmonic frequencies both in the gas phase and in aqueous solution. Solvation energies were computed by the Integral Equation Formalism-Polarizable Continuum Model (IEF-PCM)⁵, including the UAHF model. All the calculations have been performed with the Gaussian 09W series of programs⁶.

Results and Discussion

A representation of the molecular structure of DBTTC is displayed in figure 1, together with the values of the interatomic bond lengths and angles in tables 1 and 2. The results agree well with those obtained in an experimental way through X-ray diffraction.

Table-1
Interatomic Bond Lengths (in Å) for Dibenzyl Trithiocarbonate (DBTTC)

R(1-2)	1.638
R(1-3)	1.753
R(1-4)	1.746
R(3-5)	1.823
R(4-8)	1.823
R(5-6)	1.094
R(5-7)	1.091
R(5-11)	1.518
R(8-9)	1.092
R(8-10)	1.089
R(8-22)	1.511
R(11-12)	1.394
R(11-13)	1.395
R(12-14)	1.392
R(12-15)	1.080
R(13-16)	1.391
R(13-17)	1.081
R(14-18)	1.393
R(14-19)	1.079
R(16-18)	1.393
R(16-20)	1.079
R(18-21)	1.079
R(22-23)	1.397
R(22-24)	1.394
R(23-25)	1.390
R(23-26)	1.081
R(24-27)	1.394
R(24-28)	1.079
R(25-29)	1.395
R(25-30)	1.079
R(27-29)	1.391
R(27-31)	1.079
R(29-32)	1.079

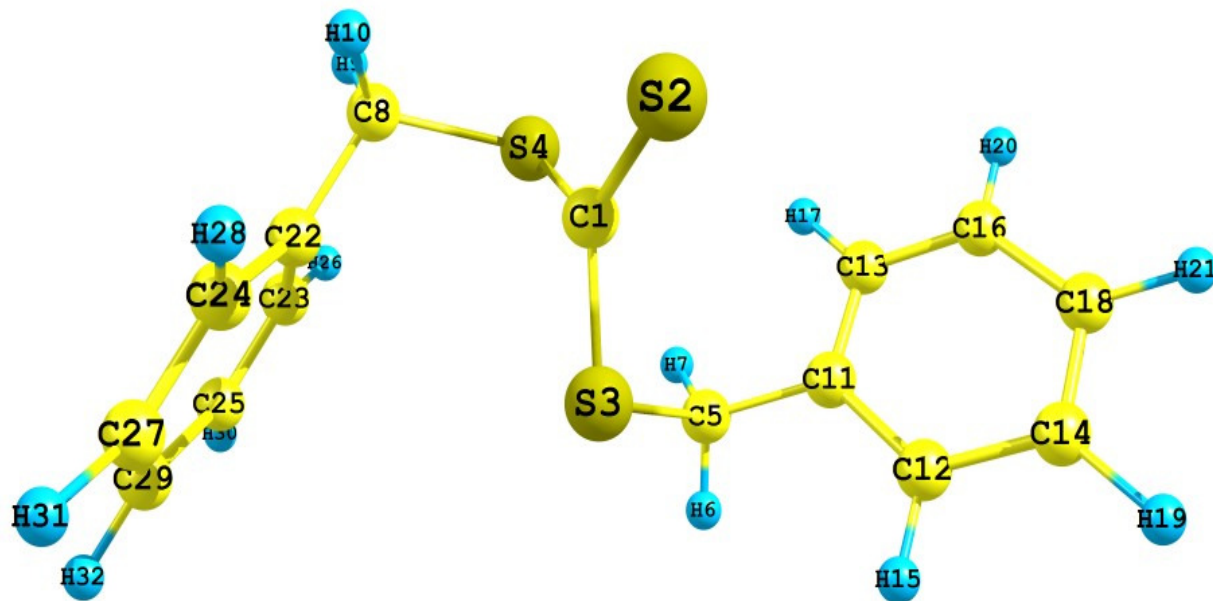


Figure-1
Molecular Structure of Dibenzyl Trithiocarbonate (DBTTC)

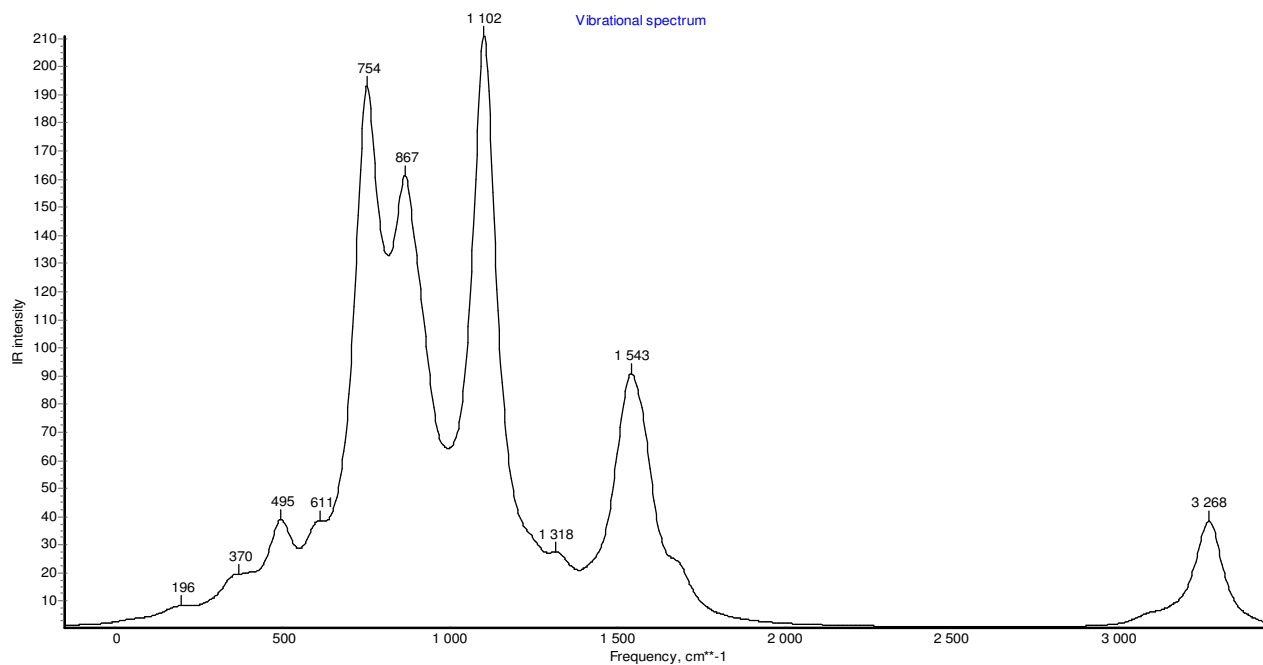


Figure-2
Vibrational Spectrum of Dibenzyl Trithiocarbonate (DBTTC)

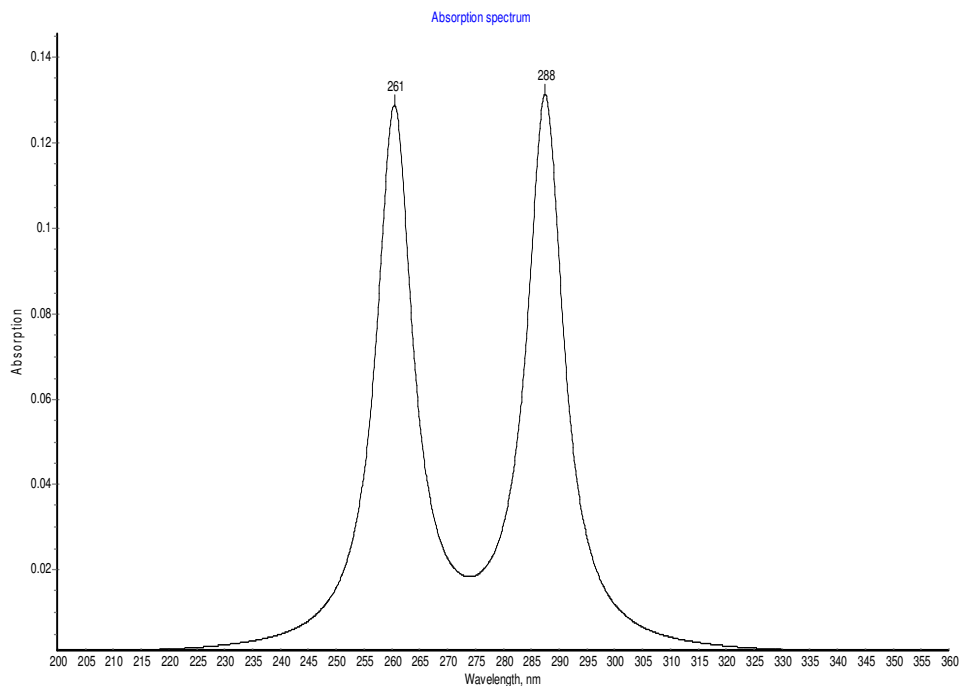


Figure-3
Absorption Spectrum of Dibenzyl Trithiocarbonate (DBTTC)

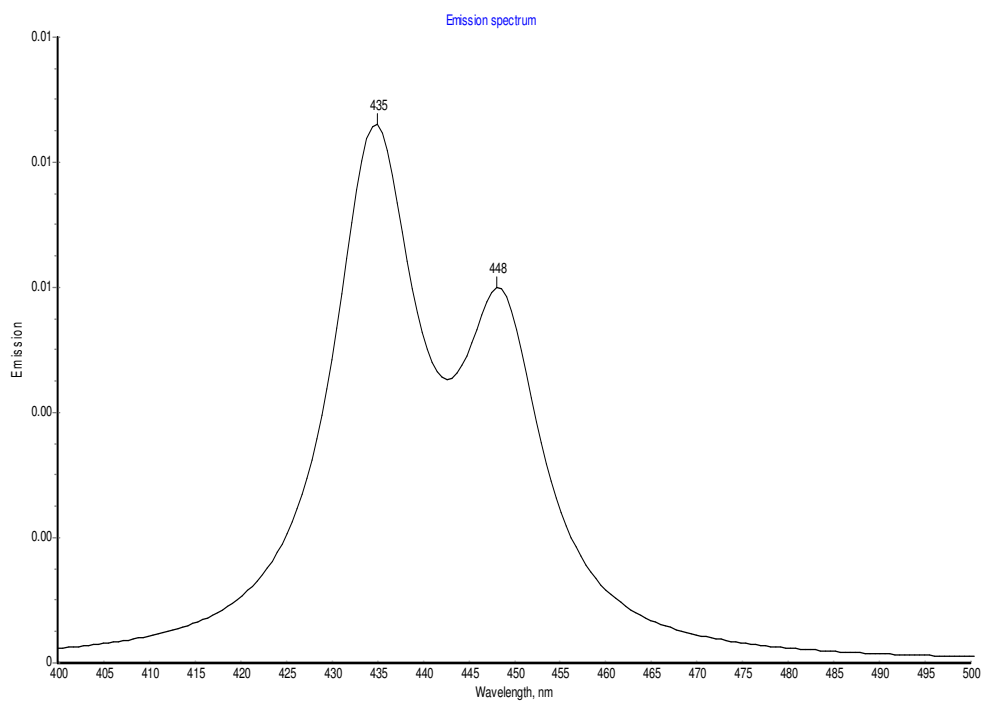


Figure-4
Emission Spectrum of Dibenzyl Trithiocarbonate (DBTTC)

Table-2
Interatomic Bond Angles (in degrees) for Dibenzyl Trithiocarbonate (DBTTC)

A(2-1-3)	117.0
A(2-1-4)	126.7
A(3-1-4)	116.2
A(1-3-5)	105.2
A(1-4-8)	101.7
A(3-5-6)	103.2
A(3-5-7)	109.5
A(3-5-11)	115.7
A(4-8-9)	104.2
A(4-8-10)	108.5
A(4-8-22)	112.6
A(6-5-7)	107.8
A(6-5-11)	109.7
A(7-5-11)	110.5
A(5-11-12)	121.6
A(5-11-13)	118.9
A(9-8-10)	109.2
A(9-8-22)	110.7
A(10-8-22)	111.4
A(8-22-24)	120.6
A(12-11-13)	119.4
A(11-12-14)	120.2
A(11-12-15)	119.5
A(11-13-16)	120.4
A(11-13-17)	119.5
A(14-12-15)	120.4
A(12-14-18)	120.3
A(12-14-19)	119.7
A(16-13-17)	120.1
A(13-16-18)	120.0
A(13-16-20)	119.9
A(18-14-19)	120.0
A(14-18-16)	119.7
A(14-18-21)	120.1
A(18-16-20)	120.1
A(16-18-21)	120.2

The calculation of the absorption spectrum (UV-Vis) of DBTTC has been performed by solving the time dependent Kohn-Sham equations according to the method implemented in Gaussian 09W⁷⁻¹⁰. The equations have been solved for 10 excited states. The geometry of the first excited state has been optimized by resorting to a HF-CIS/3-21G* calculation. The emission spectrum was thus obtained by solving again the TD-DFT equations at the same level of theory as for the absorption spectrum.

The infrared spectrum is displayed in figure 2 and shows the same peaks of the experimental determination, with a scaling factor of 0.985, which is considered acceptable for this kind of calculations.

Table-3
Dipole Moment (in Debye), Polarizability (Bohr³) and Static First Hyperpolarizability (in a.u.) for Dibenzyl Trithiocarbonate (DBTTC)

Dipole moment (field-independent basis, Debye):			
X=	-0.5070	Y=	-0.4352
Z=	-0.6259	Tot=	0.9155
Isotropic polarizability= 87.60 Bohr**3			
Static Hyperpolarizability			
K= 1 block			
1	-0.100102D+03		
K= 2 block			
1	2		
1	0.108641D+03		
2	-0.801621D+02	0.202126D+03	
K= 3 block			
1	2	3	
1	0.133385D+03		
2	-0.518882D+02	0.854917D+02	
3	0.232082D+02	0.667596D+02 0.254381	

The absorption and emission spectra of DBTTC are presented in figures 3 and 4, showing two absorption peaks at 261 and 288 nm, while there is some fluorescence because there are two emission peaks at 435 and 448 nm. The values of the dipole moment, polarizability and static first hyperpolarizability for the DBTTC molecule have been obtained after performing a POLAR calculation as implemented in the Gaussian 03W program. The results of the calculation of the Mulliken atomic charges, as well as the HOMO and the LUMO of the DBTTC molecule can be useful as a guide of the reactivity of DBTTC within the RAFT polymerization process. The dipole moment, polarizability and static first hyperpolarizability for DBTTC are presented in table 3.

Conclusions

These results show that the present model could be useful for the evaluation of reliable molecular structure and properties values for systems of interest in materials science frameworks that could be relevant for polymerization applications.

Acknowledgements

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