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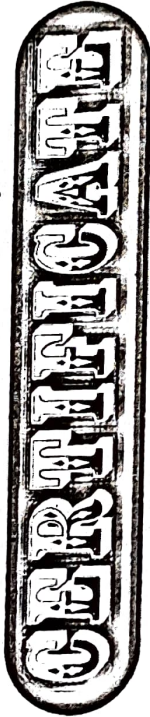
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DEPARTMENT OF PHYSICS & RESEARCH CENTRE NATIONAL SEMINAR ON FUNCTIONAL MATERIALS AND ITS APPLICATIONS



This is to certify that Mr./Ms./Dr./Prof. *V.l.k:Suma*..... *Asst.: prof*..... affiliated

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(NSFMA-2022)

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Nonlinear Optical Activity Study on 7,7,8,8-Tetra Cyano Quino Dimethane

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Abstract

The equilibrium geometry, various bonding of TCNQ compound have been performed using density functional theory(DFT) method with 6-311G (d,p) basis set. The intermolecular interaction in the TCNQ were confirmed by using NBO study. The NLO activity of molecule was confirmed by theoretical calculation

Key words: TCNQ, DFT, NBO, SHG, NLO.

1. Introduction

The nonlinear optical (NLO) materials have attracted great attention owing to their wide range of potential application in the recent technologies such as laser, optoelectronics, optical communication and data storage system (1)Kajzar et al., 2003). Recently advance in the design of novel organic molecules containing electron donor and electron acceptor moieties have aroused renewed interest in 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its derivatives (2) Nalwa et al.,1997). The present study is to understand the structural analysis of 7,7,8,8-tetra cyanoquinodimethane (TCNQ) using theoretical studies. The literature review reveals that there is no detailed study on computational techniques for the structural analysis of 7,7,8,8-tetra cyanoquinodimethane has been performed.

2. Computational Methods

Gaussian 09 software package as used for theoretical calculation. The quantum chemical calculations were performed by applying DFT method with Becke3-Lee-Yang-Parr (B3LYP) supplemented with the standard 6-311G(d,p) basis set. The optimized geometry corresponding to the minimum on the potential energy surface has been secure by solving self-consistent field equation iteratively. The detailed interpretation of the vibrational spectra was carried out with the aid of VEDA program. The polarizability first and second order hyperpolarizability were calculated using Gaussian 09 software package at B3LYP/ 6-311 G(d,p) basis set level.

3.Results and Discussion**3.1 Optimized geometry**

The optimized molecular structure of TCNQ with atom numbering scheme are shown in fig.1.1. The molecular structure of TCNQ consist of quinone ring and dicyano methane geometry. The calculated C=C(C₁-C₂,C₄-C₅) bond length of TCNQ is found to be 1.352Å .Normally C = C bond length of quinone ring is 1.322Å . This increase in bond length is due to the poor π electron orbital system of the quinone ring. It makes small positive charge in the ring carbon. All the C \equiv N bond length is observed as 1.156 Å, which shows electron withdrawing nature of the cyano group and creates high negative charge in cyano nitrogen atoms. So the cyano group shows high NLO active nature similar to the title compound.

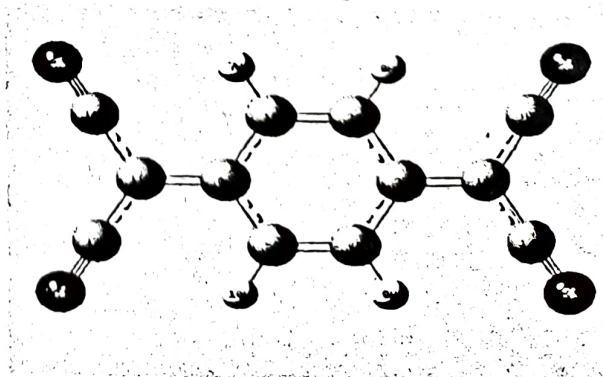


Figure 3.1 Optimized structure of 7,7,8,8-tetra cyanoquinodimethane

In $C_5-C_6-C_{11}-C_{12}$, $C_2-C_3-C_{16}-C_{19}$, and $C_4-C_5-C_{16}-C_{17}$, $C_1-C_6-C_{11}-C_{11}$ dihedral angles are 0° and 180° (Table.1c), which indicates that all compounds possess perfect co-planar nature. The calculated value of low zero point vibrational energy shows more NLO active nature of TCNQ.

3.2 NBO analysis

The DFT level computation has been used to predict the delocalization or hyperconjugation. A large number of stabilizing orbital interactions are observed in the 7,7,8,8-tetracyanoquinodimethane derivatives, most of them between vicinal NBOs and a few between terminal or remote orbital. A large $E^{(2)}$ value indicates a relatively intense interaction between the electron donor and acceptor [3].

The intramolecular interaction are formed by the orbital overlap between C-C bonding and C-N antibonding orbital which result in an intramolecular charge transfer (ICT), causing stabilization of the system. These interactions are observed as an increase in electron density in C-C, and C-N anti bonding orbitals that weaken the respective bonds. In TCNQ the most intra molecular interaction energy in $\sigma(C_5-C_{11})$ bond to antibonding $\sigma^*(C_{11}-C_{14})$ leads to the stabilization energy of 19.6 kJ/mol respectively. The stabilization energy contribution from the $\sigma(C_4-C_5) \rightarrow \sigma^*(C_5-C_6)$ interactions is 13.6 kJ/mol. The high stabilization energy shows more NLO nature of TCNQ

3.3 Charge analysis

The charge distribution of molecules have significant influence in vibrational spectra. In TCNQ, the carbon atoms C_1 , C_2 , C_4 and C_5 show low negative charge. This indicates the poor π electron system in quinone ring. In C_{12} , C_{14} , C_{17} and C_{19} there is high positive charge due to the presence of nitrogen in the corresponding carbon atoms. Due to the accommodation of electron at N_{13} , N_{15} , N_{18} and N_{20} atoms have high negative charge. All the hydrogen atoms in TCNQ have positive charge.

3.4 NLO Calculation

The average polarizability linear second order hyperpolarizability are calculated based on the finite field approach[4,5,6]. The calculated second order hyperpolarizability of TCNQ. The mean polarizability of TCNQ is 49.29×10^{-24} . The first order hyperpolarizability measures the NLO activity of the molecule. The first order hyperpolarizability of TCNQ is 16.33×10^{-33} . The second order hyperpolarizability is found to be 1.458×10^{-39} . The calculated value of polarizability, first and second order hyper polarizability shows more NLO active nature of TCNQ compounds.

4. Conclusion

The computed molecular structure geometry and vibrational spectra were in good agreement with experimental results. The low negative charge at C_1 , C_2 , C_3 , C_4 in TCNQ indicates poor π electron system. The structural activity and charge transfer interaction of NLO compounds such as 7,7,8,8-tetra cyano quino dimethane were performed using theoretical techniques. All the results conclude that 7,7,8,8 tetra cyano quino dimethane is a promising candidate for future nonlinear optical material.

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